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**PROCEEDINGS**  
**OF THE**  
**AMERICAN ACADEMY**  
**OF**  
**ARTS AND SCIENCES.**

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PROCEEDINGS  
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VOL. XV.

PAPERS READ BEFORE THE ACADEMY.

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I.

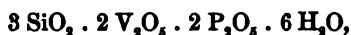
RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

BY WOLCOTT GIBBS, M. D.,

*Rumford Professor in Harvard University.*

Presented June 24th, 1879.

I PROPOSE the term "complex inorganic acid" for a class of compounds which may be considered as formed by the union of two or more acids with elimination of water in such a manner as to form a whole which in its chemical relations behaves like an acid containing a single radical. Compounds of this character were observed at an early period in the history of chemistry, but their real nature was for a long time entirely unknown, and our positive knowledge of the subject dates from the discovery of the silico-tungstates by Marignac in 1861.\* Berzelius had long before described and analyzed a compound which we should now write



the chemical relations of which are still to be studied.† He had also noticed the formation of peculiar yellow compounds when phosphoric or arsenic acids are digested with molybdic tetroxide.‡ These were again noticed and partially studied by Svanberg and Struve,§ who

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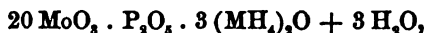
\* Ann. de Chimie et de Physique, (4,) iii. 55.

† Lehrbuch der Chemie, iii. 1058.

‡ Lehrbuch, iii. 1044.

§ K. Sv. Vet. Handlingar, 1848, p. 1.

employed a solution of ammonic molybdate as a test for the presence of phosphoric acid. Sonnenschein\* appears to have first shown that phosphoric oxide was an essential constituent of the yellow compound formed. Finally Debray assigned to the ammonium salt the formula



and separated the corresponding acid.

In a paper presented to the Association of German Naturalists and Physicians in August, 1872,† Scheibler described salts of two different phosphotungstic acids, and gave formulas for the acids themselves, as well as for a sodium salt belonging to a third series, all of which, however, he regarded as provisional. Since then nothing further has appeared upon the subject from Scheibler's pen, and I have consequently felt at liberty to include the phosphotungstates in my own work.

My investigation of the complex inorganic acids had advanced but little before I found it necessary to study the alkaline salts of tungstic acid with special care. This study has alone occupied a great deal of time, and has proved one of extraordinary difficulty, in spite of the previous labors of Laurent, Lotz, Scheibler, Zettnow, Marignac, and others. The difficulties in question are mainly these:—

1. The alkaline tungstates are numerous and unusually complex. Salts of essentially different formulas approach so closely in percentage composition, that the differences lie very near the unavoidable errors of analysis. Thus Scheibler maintains that the formula of a particular sodium salt is



while, according to Marignac, the same salt must be represented by



The analyses are hardly sufficiently close to decide the question upon purely analytical grounds.

2. Almost all the alkaline tungstates are efflorescent in a very marked degree.

3. The salts of one series agree so closely in chemical properties with those of the next, that distinctive tests are wanting, and analysis does not always suffice to distinguish two salts even when unmixed. Mixtures are naturally very hard to deal with.

\* Journal für Prakt. Chemie, liii. 842.

† Berichte der Deutschen Chem. Gesellschaft, v. 801.

4. Monoclinic and triclinic forms predominate very largely, but owing to rapid efflorescence it is very difficult to make good measurements of crystals. The resemblance between the forms of different compounds is frequently very close.

5. Many salts are decomposed by boiling, or even by hot, water, yielding two or more different salts in solution. These usually recombine in the act of crystallization or on cooling the solution, but the reactions of hot and cold solutions are often, as I shall show, very different.

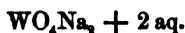
In determining the tungstic oxide in these compounds, I have employed the method of Berzelius with mercurous nitrate almost exclusively, but I have modified the process slightly so as to gain materially in accuracy. To the hot solution of the tungstate mercurous nitrate is added until in small excess. Mercuric oxide, prepared by precipitating the chloride by sodic hydrate, is then added until the yellow mercurous tungstate takes a reddish hue which is persistent after boiling. If the solution is boiled before filtering it clears rapidly, and the precipitate becomes rather more compact. The filtration and washing are then very easy and expeditious. The precipitate must be ignited as long as it loses weight. By this process Dr. Göoch, my assistant, obtained results which in two successive analyses of the same preparation rarely differed by 0.1%. The water determinations were always made by simple ignition. They almost invariably agree within a few hundredths. In the greater number of cases the alkaline base was determined from the loss, as the results obtained in this manner are far more accurate than those yielded by the direct method. But in some doubtful salts the alkali was determined directly. Ammonia was always estimated by boiling the compound with an excess of sodic hydrate, collecting the ammonia in chlorhydric acid, and weighing it as chloride.

The only objection to the method of determining tungstic oxide above given is, that the precipitate of mercurous tungstate is rather voluminous, so that it is necessary to work with quantities of alkaline tungstate not much exceeding one gramme in weight. I endeavored to overcome this difficulty by omitting the mercuric oxide and evaporating the solution and precipitate, after the addition of mercurous nitrate, to perfect dryness in a water bath, continuing the heat until all the free nitric acid was expelled. This method gave results which corresponded very closely with those obtained by the use of mercuric oxide to neutralize the free nitric acid, and in consequence of the extremely compact form of the dry mercurous tungstate, permitted the

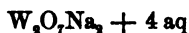
employment of much larger quantities of salt for analysis. On the other hand, it presents another difficulty, arising from the fact that the dry mercurous tungstate adheres with excessive tenacity to the evaporating vessels, whether of glass, porcelain, or platinum, so that the first method is on the whole to be preferred.

The separation of tungstic oxide from other bases is best effected by fusing the salt with an excess of potassio-sodic carbonate and dissolving out the alkaline tungstates formed.

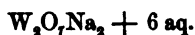
Normal sodic tungstate has long been known, and all the analyses concur in assigning to it the formula



It is now to be had from various German firms in a state of purity, and forms the most convenient material for the study of the compounds of tungsten. The acid salt analyzed by Anthon, and to which the formula



was long ascribed, is now well known to have an entirely different composition; but Lefort\* has recently endeavored to show that ditungstates and tritungstates really exist, and has described a number of salts of each series. Lefort obtains sodic ditungstate by adding glacial acetic acid to a saturated solution of the neutral salt until the reaction with litmus becomes acid. After a day or two the salt separates in long prismatic crystals, with the formula



I have repeatedly attempted to prepare the ditungstate by this process, but without success in any one instance, the resulting salts being, as I shall show further on, in all cases very different in composition. Lefort prepared sodic tritungstate by pouring a concentrated solution of the ditungstate into a boiling solution of glacial acetic acid. His analyses agree fairly well with his formulas, and I have adopted his results without question, in the belief that my own inability to reproduce them was due to the omission in his paper of some matter of detail which appeared insignificant, but which was really important.

*Ten to Four Sodium Salt.*—The salt to which I have given this name appears to have been first observed by Forcher,† who obtained

---

\* Ann. de Chimie et de Physique, (5,) ix. 93.

† Wiener Akad. Berichte, xlv. 2, 177.



it by passing a current of carbonic dioxide for some days through a solution of the normal tungstate. Forcher gives the formula



and suggests, though without adducing any evidence in support of his view, that it may be a double salt, with the formula



Marignac, who appears to have been unacquainted with Forcher's paper, soon afterward described the same salt as an accidental product, attributing to it the formula



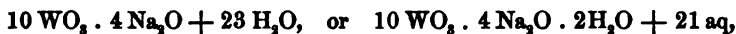
Finally, Lefort\* obtained it by the action of acetic acid upon a solution of the normal tungstate, and, without citing the results of Forcher, also proposed the formula



I have obtained the salt by the following process, which appears to be the most convenient. Normal sodic tungstate,



is to be dissolved in water, and acetic acid added, in small portions at a time, to the boiling solution, until the reaction becomes strongly acid. Alcohol then precipitates the 10:4 tungstate as a heavy oil, which soon becomes a solid mass. The solution on standing some days deposits colorless crystals, which are usually much twinned, and, according to Marignac, belong to the monoclinic system. They effloresce readily in dry air and are soluble, according to Forcher's determination, in 12.6 parts of water at 22° C. When heated they fuse to a yellow liquid, which on cooling gives a white crystalline mass nearly insoluble in cold water but dissolved by long boiling. I assign to the crystallized hydrate the formula



with which all the analyses agree very closely. Of the salt,

I.	1.4152 gr. lost 0.1963 gr. by ignition	= 13.88%
	0.4095 gr. gave 0.3194 gr. $\text{WO}_3$	= 77.99%
II.	1.1182 gr. lost on ignition 0.1558 gr. water	= 13.94%
	0.8950 gr. gave 0.6968 gr. $\text{WO}_3$	= 77.85%

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\* Loc. cit.

- III.  $\begin{cases} 1.3594 \text{ gr. lost on ignition } 0.1862 \text{ gr. water} = 13.70\% \\ 0.5340 \text{ gr. gave } 0.4155 \text{ gr. } \text{WO}_3 = 77.80\% \end{cases}$
- IV.  $\begin{cases} 1.1660 \text{ gr. lost on ignition } 0.1624 \text{ gr. water} = 13.93\% \\ 0.5981 \text{ gr. gave } 0.4659 \text{ gr. } \text{WO}_3 = 77.89\% \end{cases}$
- V.  $\begin{cases} 1.3594 \text{ gr. lost on ignition } 0.1862 \text{ gr. water} = 13.70\% \\ 0.5340 \text{ gr. gave } 0.4155 \text{ gr. } \text{WO}_3 = 77.80\% \end{cases}$

The formula  $10 \text{ WO}_3 \cdot 4 \text{ Na}_2\text{O} + 23 \text{ aq}$  requires

		Calc'd.	1.	2.	3.	4.	5.	Forcher.	Marignac.
10 WO <sub>3</sub>	2320	77.80	77.99	77.85	77.80	77.89	77.80	77.82	77.88
4 Na <sub>2</sub> O	248	8.32	8.13	8.21	8.50	8.18	8.50	8.16	8.39
23 H <sub>2</sub> O	414	13.88	13.88	13.94	13.70	13.93	13.70	13.88	13.53
	2982	100.00						99.86	99.80

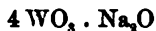
The means of all these analyses may be compared with the three formulas above given.

		$\text{WO}_3$	$\text{Na}_2\text{O}$	$\text{H}_2\text{O}$
For the ratio	10 . 4 . 22	78.27	8.37	15.36
"	" 10 . 4 . 24	77.63	8.16	14.21
"	" 10 . 4 . 23	77.80	8.32	13.88
Means of new analyses,		77.86	8.30	13.83

The analyses therefore leave no reasonable doubt as to the true constitution of the salt. The solution of the 10:4 sodic tungstate has a distinct acid reaction, but it is very difficult to determine the limits of the basicity in this series, because no salts could be obtained having a number of molecules of fixed base higher than four. On the other hand, the white insoluble mass obtained by igniting the crystalline hydrate must have the formula



and I consider it a true pyro-salt. When boiled for some time with water, the pyro-salt dissolves and the original salt crystallizes from the solution. The case appears to be exactly analogous to that of sodic metatungstate, the insoluble



of Scheibler and Marignac, giving the normal sodic metatungstate,



when heated with water in a sealed tube. The reactions of the 10:4 salt with metallic solutions are extremely similar to those of the 12:5 salt,



so that in fact it is difficult to distinguish between the two in any other way than by the habitus of the crystals and by analysis.

When the 10 : 4 salt is dissolved in water and a current of sulphydric acid gas passed into the solution to the point of saturation, the liquid becomes at first yellow, and finally orange red. On standing or evaporation, it deposits brown tungstic sulphide,  $WS_3$ , and the still faintly yellow mother liquor gives fine colorless triclinic crystals, which are separate and distinct, not twinned or aggregated in masses like the 10 : 4 salt. These crystals after recrystallization have the formula of the 12 : 5 salt presently to be described, namely,

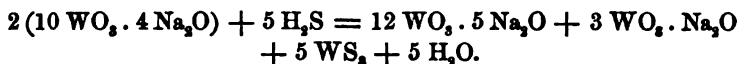


as the following analyses show :—

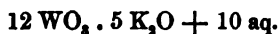
1.6491 gr. gave	1.2760 gr. $WO_3$	= 77.38%
2.3696 gr. lost	0.3308 gr. water	= 13.96%
2.0037 gr. "	0.2790 gr. "	= 13.92%

		Calc'd.	Found.
12 $WO_3$	2784	77.38	77.38
5 $Na_2O$	330	8.61	8.68
28 $H_2O$	504	14.01	13.92 13.96
	<u>3618</u>	<u>100.00</u>	

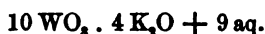
The formation of the 12 : 5 from the 10 : 4 salt is easily explained, as well as the separation of the tungstic sulphide, since we have



A concentrated solution of the 10 : 4 sodium salt is resolved by boiling into the 12 : 5 salt and other compounds difficult to isolate in a state of purity. When a hot solution of potassic bromide or nitrate is added to a boiling solution of the 10 : 4 sodium salt, a white crystalline precipitate is speedily formed, which has the formula



But if a cold solution of a potassic salt is added to a cold solution of the 10 : 4 sodium salt, a white crystalline precipitate is formed, which has the formula



*Twelve to Five Sodium Salt.* — This is the salt to which Scheibler gives the formula



and which Marignac writes



According to Lotz, the salt contains fourteen atoms of water in place of sixteen as found by Scheibler. I have adopted the formula of Marignac, which agrees best with the analyses. In preparing this salt I have employed Scheibler's method, which consists in nearly neutralizing a boiling solution of the neutral tungstate,  $\text{WO}_4\text{Na}_2 + 2 \text{ aq.}$  by chlorhydric acid. When the proper quantity of chlorhydric acid is added, the 12 : 5 salt is formed at once, and crystallizes from the solution in large colorless crystals, which, according to Scheibler, are monoclinic; according to Marignac, triclinic. If the proportion of chlorhydric acid is just sufficient to give an onion-red reaction with litmus, crystals are obtained, which are either a combination or a mixture of equal molecules of the 10 : 4 and 12 : 5 salts. These crystals are, according to Dr. Gooch, triclinic; their habitus resembles that of the 12 : 5 rather than that of the 10 : 4 salt. In this salt, in two different preparations carefully dried and pressed with woollen paper,

I.	{	1.2546 gr. gave	0.9725 gr. $\text{WO}_3$	= 77.51%
		1.2320 gr. "	0.9554 gr. "	= 77.55%
		1.4680 gr. lost	0.2035 gr. water	= 13.86%
		1.7511 gr. "	0.2481 gr. "	= 13.88%
II.	{	1.0842 gr. gave	0.8407 gr. $\text{WO}_3$	= 77.54%
		1.0908 gr. "	0.8450 gr. "	= 77.47%
		1.6919 gr. lost	0.2362 gr. water	= 13.96%
		1.5259 gr. "	0.2125 gr. "	= 13.93%

The analyses agree closely with the formula



or,



which requires

		Calc'd	Mean	Found.			
22 $\text{WO}_3$	5104	77.57	77.52	77.51	77.55	77.54	77.47
9 $\text{Na}_2\text{O}$	558	8.48	8.57	...	...	...	...
51 $\text{H}_2\text{O}$	918	13.95	13.91	13.86	13.88	13.96	13.93
	6580	100.00	100.00				

I have already stated, that in repeated trials I had not been able to obtain the sodic ditungstate described and analyzed by Lefort, though the process given by him was followed implicitly. In one experiment the crystals obtained gave on analysis results which correspond closely with the formula



1.9868 gr. lost on ignition	0.2786 gr. water	= 14.02%
1.2870 gr. " "	0.1806 gr. " "	= 14.01%
0.9365 gr. gave	0.7243 gr. $\text{WO}_3$	= 77.34%
1.3560 gr. " "	1.0483 gr. " "	= 77.31%

	Calc'd.	Found.
12 $\text{WO}_3$	77.88	77.34 77.31
5 $\text{Na}_2\text{O}$	8.61	8.66
28 $\text{H}_2\text{O}$	14.01	14.02 14.01
	<u>100.00</u>	

In this experiment the normal tungstate was dissolved in cold water to a very strong solution, glacial acetic acid was added in excess, and the whole allowed to stand for twenty-four hours, when prismatic crystals separated. In a second experiment a concentrated solution of sodic tungstate was heated to the boiling point and ordinary acetic acid added in excess. Alcohol then threw down a pasty mass, which, after re-solution in water and crystallization, gave on analysis results which corresponded with the formula



1.0861 gr. lost on ignition	0.1492 gr. water	= 13.74%
1.3830 gr. " "	0.1895 gr. " "	= 13.70%
0.8884 gr. gave	0.6899 gr. $\text{WO}_3$	= 77.66%
1.2746 gr. " "	0.9902 gr. " "	= 77.69%

	Calc'd.	Found.
22 $\text{WO}_3$	77.57	77.67 77.69
9 $\text{Na}_2\text{O}$	8.48	8.60
51 $\text{H}_2\text{O}$	13.95	13.70 13.74
	<u>100.00</u>	

The small differences between the calculated formula and the direct results of the analyses, in this instance, are exactly such as would be produced by the admixture of a small percentage of the 10:4 sodium salt, which, as I have shown above, is formed when a solution of neutral sodic tungstate is boiled for some time with an excess of acetic acid.

The general result of my own study of the action of acetic acid upon the neutral tungstate is, that we obtain the 12:5, the 22:9, or the 10:4 salt, according to the circumstances of the case, the constitution of the salt formed depending mainly upon the degree of concentration of the acid and upon the duration of its action. These results are in no way inconsistent with those of Lefort, and his analyses seem to leave no reasonable doubt that he obtained various salts to be classed as ditungstates and tritungstates.

*Potassic Tungstates.* — When a hot solution of the 10:4 sodium salt is mixed with a hot solution of potassic nitrate, a white precipitate shortly appears in small colorless crystalline scales, which may be recrystallized by projecting them in very small quantities at a time into boiling water. This method, which was first given by Scheibler, enables us to redissolve the salt in water without loss from the excessively violent succussions which occur on heating the salt with water in the usual manner. The salt requires a rather large quantity of water for solution, and crystallizes almost completely from the cold liquid. Of this salt in the first preparation, —

0.9888 gr. lost on ignition	0.0510 gr. water	= 5.18%
0.6513 gr. " "	0.0358 gr. " "	= 5.49%
1.1663 gr. " "	0.0610 gr. " "	= 5.23%
1.1287 gr. " "	0.0596 gr. " "	= 5.28%
1.0068 gr. gave	0.8173 gr. $\text{WO}_3$	= 81.21%

In a second preparation, —

1.4312 gr. lost on ignition	0.0751 gr. water	= 5.25%
1.5846 gr. " "	0.0832 gr. " "	= 5.25%
0.5786 gr. gave	0.4686 gr. $\text{WO}_3$	= 80.99%
0.4773 gr. " "	0.3875 gr. " "	= 81.20%
1.8957 gr. " "	1.5370 gr. " "	= 81.08%

These analyses lead to the formula



which requires :—

		Calc'd.	Mean.	1.	Found.	2.	
12 $\text{WO}_3$	2784	81.02	81.12	81.21	80.99	81.20	81.08
5 $\text{K}_2\text{O}$	472	13.73	13.62	...	...	...	...
10 $\text{H}_2\text{O}$	180	5.25	5.26	5.29*	5.25	5.25	...
	3436	100.00					

\* Mean of the four determinations of water in the first preparation.

Marignac gives eleven molecules of water. Scheibler gives the formula  $7 \text{WO}_3 \cdot 3 \text{K}_2\text{O} + 6 \text{aq}$ , but his analyses agree better with that of Marignac.

When normal potassic tungstate,  $\text{WO}_4\text{K}_2$ , is evaporated to dryness with boric hydrate, and the soluble salts are washed out from the mass, a salt is obtained which after recrystallization has the formula



The same salt is formed when cold solutions of potassic nitrate or bromide are added to cold solutions of the 10:4 sodium salts. It resembles the 12:5 potassium salt, already described, so closely, that it is difficult to distinguish between the two. This salt has not been described by other writers upon the subject. In preparation *a*, from the action of boric acid upon normal potassic tungstate,

0.4566 gr. gave	0.3714 gr. $\text{WO}_3$	= 81.34%
0.5915 gr. lost on ignition	0.0331 gr. water	= 5.59%

In preparation *b*, from the action of acetic acid upon the normal potassium salt,

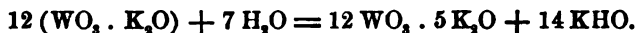
0.7418 gr. gave	0.6024 gr. $\text{WO}_3$	= 81.21%
1.1104 gr. lost on ignition	0.0610 gr. water	= 5.49%
0.7060 gr. gave	0.5736 gr. $\text{WO}_3$	= 81.27%
1.0266 gr. lost on ignition	0.0556 gr. water	= 5.42%

These analyses correspond best with the formula



		Calc'd.	Mean.			
10 $\text{WO}_3$	2320	81.13	81.27	81.34	81.2	81.27
4 $\text{K}_2\text{O}$	377.6	13.20	13.23	13.07	13.30	13.31
9 $\text{H}_2\text{O}$	162	5.67	5.50	5.59	5.49	5.42
	<u>2859.6</u>	<u>100.00</u>				

It is probable that the salt had lost a little water by efflorescence. When normal potassic tungstate is dissolved in boiling water, it is decomposed into free alkali and 12:5 acid tungstate. The decomposition may be represented by the equation,



In the acid salt formed in this manner,

0.7738 gr. lost on ignition	0.0414 gr. water	= 5.35%
1.0385 gr. gave	0.8411 gr. $\text{WO}_3$	= 80.99%

The formula  $12 \text{WO}_3 \cdot 5 \text{K}_2\text{O} + 10 \text{aq}$  requires 81.02%  $\text{WO}_3$  and 5.25%  $\text{H}_2\text{O}$ .

*Ammonic Tungstates.*—When a solution of ammonic chloride is added to one of the 10 : 4 sodic tungstate, beautiful white talcose scales are thrown down, which are but slightly soluble in cold water. After washing, they may be dissolved in boiling water without evolution of ammonia and recrystallized. The analyses of this salt agree fairly well with the formula



as the following analyses show :—

I. {	0.5658 gr. gave	0.4851 gr. $\text{WO}_3$	= 85.74%
	0.5602 gr. lost on ignition	0.0690 gr. water and ammonia	= 12.31%
II. {	0.3846 gr. lost	0.0427 gr. " "	= 12.77%
	0.3849 gr. gave	0.3294 gr. $\text{WO}_3$	= 85.59%

		Calc'd.	Mean.	Found.	
50 $\text{WO}_3$	11600	85.42	85.62	85.74	85.59
4 $\text{Na}_2\text{O}$	248	1.83	1.79	1.94	1.64
16 $(\text{NH}_4)_2\text{O}$	832	6.12	12.54	12.31	12.77
50 $\text{H}_2\text{O}$	900	6.63			
	13580	100.00	99.95		

Analyses (I.) and (II.) are of different preparations of the same salt. When commercial ammonic tungstate (containing a little sodic oxide) is dissolved in ammonia, and acetic acid is added to the filtered liquid, a white slightly soluble salt is obtained which after recrystallization has the formula



In this salt :

0.9293 gr. lost on ignition	0.1087 gr.	= {	11.69% $\text{NH}_3$ and $\text{H}_2\text{O}$
			88.31% $\text{WO}_3$
0.5866 gr. " "	0.0626 gr.	= {	11.66% $\text{NH}_3$ and $\text{H}_2\text{O}$
			88.34% $\text{WO}_3$
0.6602 gr. gave	0.2039 gr. platinum	=	8.15% $(\text{NH}_4)_2\text{O}$
1.1241 gr. " "	0.3870 gr. " "	=	7.92% " "

		Calc'd.	Mean.	Found.	
12 $\text{WO}_3$	2784	88.32	88.32	88.34	88.31
5 $(\text{NH}_4)_2\text{O}$	260	8.24	8.03	8.15	7.92
6 $\text{H}_2\text{O}$	108	3.44	3.64	3.51	3.77
	3152	100.00	99.99		



Marignac found in this salt five molecules of water. Lotz and Scheibler gave it the formula



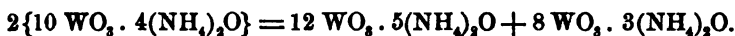
Marignac has also described and analyzed an ammonium salt to which he gives the formula



I should double this formula, and write it



so that it would then belong to the series of 10:4 salts, the existence of which I have endeavored to establish. According to Marignac, it breaks up by solution in water into the 12:5 and 8:3 salts.



*Zinc Salts.*—When a solution of zincous sulphate is added in small excess to a hot solution of the 10:4 sodic tungstate, no precipitate is produced at first, but after a few seconds beautiful aggregates of white needles make their appearance, and continue to be deposited for some time. They are almost perfectly insoluble in boiling water. For analysis they were washed with cold water and dried in pleno over sulphuric acid. The zinc salt is soluble both in an excess of zincous sulphate and of sodic tungstate; hence the precipitate which is at first formed is instantly redissolved and does not become permanent until a small excess of the sulphate is added. In this salt,

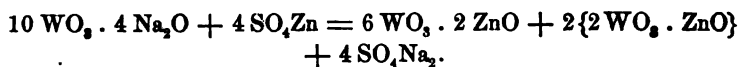
0.3342 gr. lost on ignition	0.0349 gr. water	= 10.44%
0.6392 gr. gave	0.5128 gr. $\text{WO}_3$	= 80.50%
1.0205 gr. “	0.8200 gr. “	= 80.35%

These analyses correspond with the formula



		Calc'd.		Found.
6 $\text{WO}_3$	1392	80.27	80.50	80.35
2 $\text{ZnO}$	162	9.34		9.14 (loss)
10 $\text{H}_2\text{O}$	180	10.39	10.44	
	<u>1734</u>	<u>100.00</u>		

From this it appears that the zinc salt is formed by the decomposition of the 10:4 sodic tungstate. The result may be expressed by the equation,

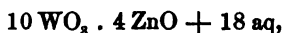


The zincous ditungstate, as Lefort has shown, is readily soluble in water and remains in solution.

When a cold solution of zincous sulphate is added to a cold solution of the 10:4 sodium salt, a different result is obtained. A white precipitate is at first formed as before, which instantly redissolves. After a small excess of the sulphate has been added, the solution gives in a short time colorless needles of a second zinc salt. Like the 6:2 salt first described, this is insoluble in water, cold or hot, but readily dissolves in an excess of the tungstate or sulphate. When a large excess of the sulphate is present, the zincous tungstate does not separate from the solution. Of this salt in one preparation, dried over  $\text{SO}_4\text{H}_2$ :

0.6586 gr. lost on ignition	0.0706 gr. water	= 10.72%
0.5894 gr. gave	{ 0.0638 gr. ZnO	= 10.82%
	{ 0.4606 gr. $\text{WO}_3$	= 78.16%

These analyses lead to the formula

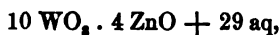


which requires

		Calc'd.	Found.
10 $\text{WO}_3$	2320	78.16	78.16
4 ZnO	324	10.92	10.82
18 $\text{H}_2\text{O}$	324	10.92	10.72
	<u>2968</u>	<u>100.00</u>	<u>99.70</u>

In a second preparation of the same salt, dried by woollen paper, 1.0006 gr. gave by ignition 0.1668 gr. water, also 0.7322 gr.  $\text{WO}_3$  and 0.1048 gr. ZnO = 16.62% water, 73.18%  $\text{WO}_3$ , and 10.47% ZnO.

These results correspond to the formula

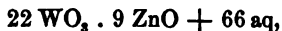


which requires

		Calc'd.	Found.
10 $\text{WO}_3$	2320	73.27	73.18
4 ZnO	324	10.24	10.47
29 $\text{H}_2\text{O}$	522	16.49	16.62
	<u>3166</u>	<u>100.00</u>	<u>100.27</u>

When a cold solution of zincous sulphate is added to a cold solution of the 22-atom sodium salt a precipitate is formed, which re-

dissolves precisely as in the last-mentioned cases. After the solution of zinc has been added in small excess, white needles separate, which are insoluble in water, and have the formula



as the following analyses show :

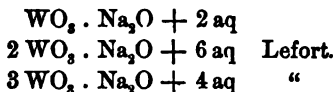
1.4620 gr. gave 0.2509 gr. water on ignition, 1.0602 gr.  $\text{WO}_3$  and 0.1508 gr.  $\text{ZnO} = 17.16\%$  water,  $72.52\%$   $\text{WO}_3$ , and  $10.31\%$   $\text{ZnO}$ .

		Calc'd.	Found.
22 $\text{WO}_3$	5104	72.69	72.52
9 $\text{ZnO}$	729	10.38	10.31
66 $\text{H}_2\text{O}$	1188	16.93	17.16
	<u>7021</u>	<u>100.00</u>	<u>99.99</u>

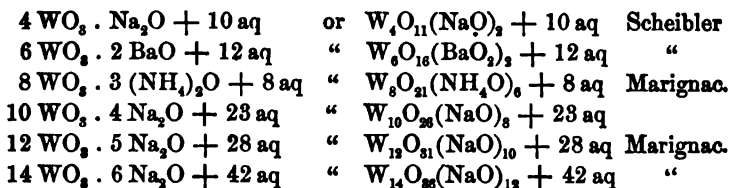
The salt was dried for some time upon woollen paper.

*General Conclusions.*—From my own investigations, as well as from those of other chemists who have preceded me, I arrive at the following classification of the alkaline tungstates as most nearly representing the present state of our knowledge. There are three series of salts, which may be termed respectively normal tungstates, meta-tungstates, and pyro-tungstates. The two first-named series may be represented by the following as typical salts :—

#### *Normal Series.*



#### *Meta-Tungstates.*



The salts of the normal series require no special notice. As already stated, I have not succeeded in preparing the di- and tri-salts of Lefort, but there seems to be no reason to doubt their existence. The pyro-salts are obtained from the meta-salts by ignition, as insoluble crystalline masses, which are decomposed by long boiling with water. All the

meta-tungstates with an alkaline base, appear to contain water of constitution and to have an acid reaction, but it is difficult to determine the quantity of basic hydrogen with certainty, and the mere fact that the salts have an acid reaction is not in itself conclusive evidence that they are in the strict chemical sense *acid*. Tungstates have been described by different chemists, which do not fall within either of the groups given above. In all these cases, however, it will be found on examination, that the analyses do not agree well with the formulas assigned, and that there is reason to believe that the salts studied were mixtures. I consider it at least probable that the tri-salts of Lefort belong in reality to the meta-series, their molecular weights being doubled. But it is of course possible that we have here cases of isomerism, and I much regret that I did not succeed in obtaining these salts for study and comparison. With respect to the double salt which I have described above, and which has the formula



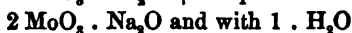
I may remark that it is possible that the compound is really



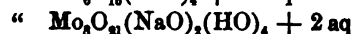
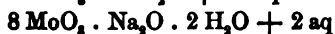
and that it is not a double salt, but one term in a series which we obtain by again doubling the formulas of the meta-tungstates as I have given them above. The question is one which I must leave undecided for the present at least.

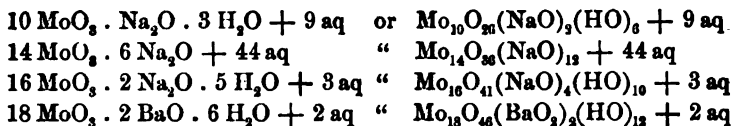
The analogy between the compounds of tungsten and molybdenum is in general so great, that we ought to expect to find alkaline molybdates corresponding to the three series of tungstates. We owe to Ullik the most complete examination of the molybdates which has been published. A careful study of his results will show that, while we have a number of molybdates to which there are apparently no corresponding tungstates, we have at least reason to believe in the existence of the three series of normal, meta, and pyro salts. Thus the following salts may be assumed as typical:—

*Normal Series.*

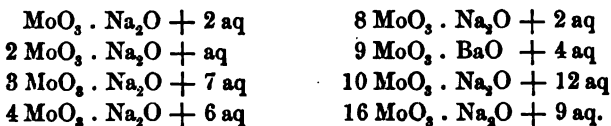


*Meta Series.*

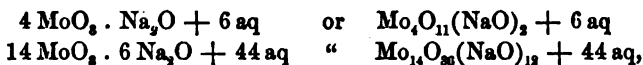




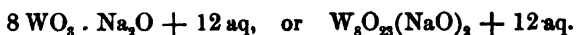
It may of course be maintained that the arrangement of the acid salts of molybdic oxide which I have adopted is purely arbitrary, and that they might be written with equal or greater probability in the usual manner, as members of the normal series, which would then be :



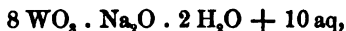
To this I reply that one arrangement is no more arbitrary than the other, since we have no positive knowledge of the constitution of these salts, their molecular weights being, as in the case of most inorganic compounds, entirely unknown. The commonly received view is therefore also a pure assumption. In any case, however, we have the two salts, represented respectively by the formulas



forming the upper and lower limits of a molybdic series corresponding to alkaline tungstates, and from these we may fairly infer the existence of the intermediate compounds. But one acid tungstate of the meta series is at present known, the salt



This may be considered as an acid salt of the 8-atom term, and written

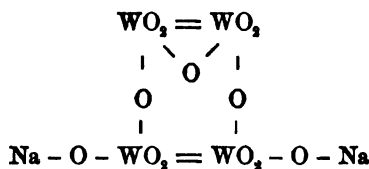


so that it will correspond to the molybdic salt

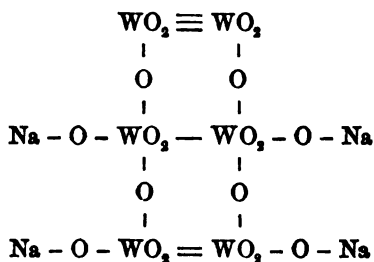


But the supposition that acid metatungstates of the 4 : 1 series really exist, is in no way inconsistent with the view of the whole subject which I have taken. So far as I know, no attempt has been made to exhibit the mode of union of the elements in the higher tungstates. Our views of the subject will differ according as we consider tungsten

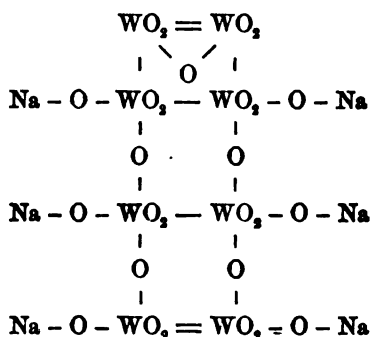
as tetratomic or hexatomic. In what follows I have adopted the latter hypothesis, partly because the hexatomic character of tungsten is well marked in various compounds, as for example in  $\text{WCl}_6$ , and partly because the graphical representations are, on the whole, simpler. Moreover, if we consider tungsten to be tetratomic in the normal series, we obtain a reason for the existence and peculiar character of the meta series, by supposing that in this the metal is hexatomic. We may, to begin with, represent sodic metatungstate,  $4 \text{WO}_3 \cdot \text{Na}_2\text{O}$ , as follows :



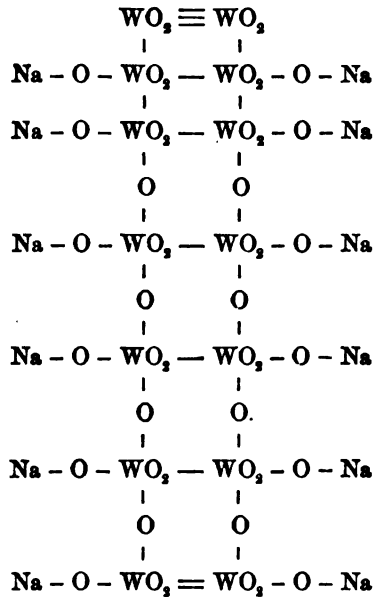
The next term in the series,  $6 \text{WO}_3 \cdot 2 \text{Na}_2\text{O}$ , will then be



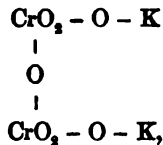
The third term,  $8 \text{WO}_3 \cdot 3 \text{Na}_2\text{O}$ , may be represented by the graphical formula



and so on for the other known terms, the highest,  $14 \text{WO}_3 \cdot 6 \text{Na}_2\text{O}$ , being represented by the expression

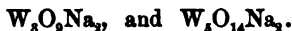


It will be seen that, with this view of the subject, those terms in the series in which the number of atoms of sodic oxide is even are represented by formulas in which the free atoms of  $\text{WO}_3$  are united, in part directly, and in part by oxygen, while the union is direct when the number of atoms of sodic oxide is odd. I shall return to this subject in speaking of the phosphotungstates and other complex inorganic acids. No great value can, in the present state of our knowledge, be attributed to formulas like the above. They afford, however, some assistance in showing the possible mode of formation of the different terms of the series, but various other constructions may be devised which are perhaps equally probable. In adopting provisionally the particular construction which I have used, I have simply followed the clew given by the commonly received formula for potassic dichromate,

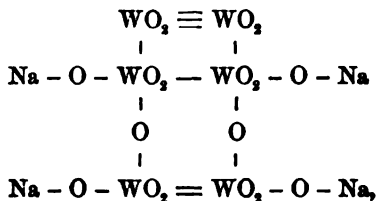


which of course gives a similar expression for the homologizing term in the acid tungstate series. So far as I am aware, no attempt

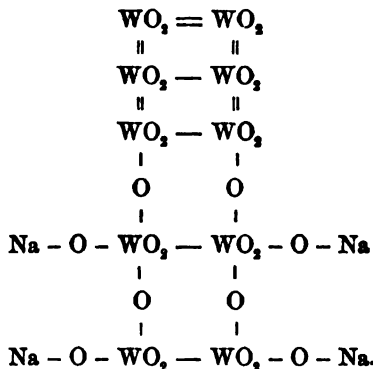
has been made to formulate the remarkable compounds of tungsten described by Wöhler and others, and which may be expressed empirically by the formulas



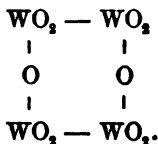
If we double these formulas, we may bring them into harmony with the series of acid tungstates by writing them respectively,



and



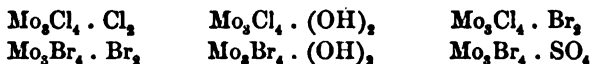
These formulas, if like the others purely hypothetical, have at least the merit of explaining the production of the insoluble sodium salts in a simple and natural manner. They are also entirely consistent with the simplest view which we can adopt with respect to the constitution of the blue oxide of tungsten, which is commonly written  $W_3O_9$ , but which is much more probably  $W_4O_{10}$ , and structurally



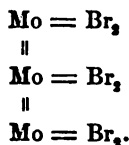
The progress of science tends to show that the constitution of inorganic compounds is more complex than would at first appear. It would not be difficult to multiply instances which support this view,



but I shall content myself with citing a single case, which has not been discussed, and which, strangely enough, has attracted but little attention. I refer to the remarkable series of compounds of molybdenum studied by Blomstrand\* and by Atterberg.† Representative terms in this series are expressed by the formulas



omitting water of crystallization for greater brevity. The action of alkalis upon the bromide  $\text{Mo}_3\text{Br}_4 \cdot \text{Br}_2$  produces first  $\text{Mo}_3\text{Br}_4 \cdot (\text{OH})_2$ , and afterward  $\text{Mo}_3(\text{OH})_4(\text{OH})_2$ , or  $\text{Mo}_3(\text{OH})_6$ , the hydrate of the protoxide of molybdenum, usually written  $\text{MoO} \cdot \text{OH}_2$ , or  $\text{Mo}(\text{OH})_2$ . There is therefore good reason to believe that the lowest expression for this hydrate is  $\text{Mo}_3(\text{OH})_6$ , the structural formula of the corresponding bromide being, perhaps,



In this formula the end atoms of molybdenum are tetratomic, and the middle atom hexatomic, which will perhaps explain the fact that there are but two movable atoms of bromine in a whole series of salts. If molybdic protoxide is  $\text{Mo}_3\text{O}_3$ , it is probable that the teroxide is not  $\text{MoO}_3$ , but rather some higher multiple of this expression, and we may extend the inference to  $\text{WO}_3$  also.

With these preliminaries, I pass to the special subject of my work.

\* Journal für prakt. Chemie, lxxxii. 436.

† Några bidrag till Kännedomen om Molybden, Stockholm, 1872, p. 16.

(To be continued.)

## II.

CONTRIBUTIONS FROM THE PHYSIOLOGICAL LABORATORY OF  
THE HARVARD MEDICAL SCHOOL.

## A NEW FORM OF PLETHYSMOGRAPH.

By H. P. BOWDITCH, M.D.

Presented May 14, 1879.

A PROBLEM which frequently presents itself to physiologists is that of measuring the changes in the size of organs, either hollow or solid, which are produced by variations in the conditions to which they are subjected. The simplest way of doing this is to fill the organ with fluid, if it is hollow, or to place it in a closed vessel containing fluid, if it is solid, and to allow the fluid thus contained within or surrounding the organ to communicate with a small glass tube, in which its rise and fall furnishes a measure of the changing size of the organ under observation. It is evident, however, that this rise or fall of the fluid changes the pressure to which the organ is subjected, and that this change of pressure, by affecting the size of the organ, introduces an error into the observation.

The Plethysmograph is an instrument devised to meet this difficulty. Its essential part is a contrivance by which the fluid is allowed to flow freely to and from the organ to be measured without changing its absolute level in the receptacle into which it flows, while at the same time a record is made of the volume of the fluid thus displaced.

The problem was successfully solved by Mosso,\* who supported the receptacle for the fluid coming from the organ to be measured by letting it float in a liquid the specific gravity of which was so adjusted that any rise of fluid in the receptacle was counterbalanced by the sinking of the receptacle in the liquid in which it floated. Von Basch† accomplished the same object by suspending the receptacle for the fluid from one arm of a balance counterpoised in such a way that the weight of the fluid entering the receptacle caused the latter to sink by an amount precisely equal to the rise of the fluid within it.

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\* Arbeiten aus der phys. Anstalt zu Leipzig, 1874, p. 156.

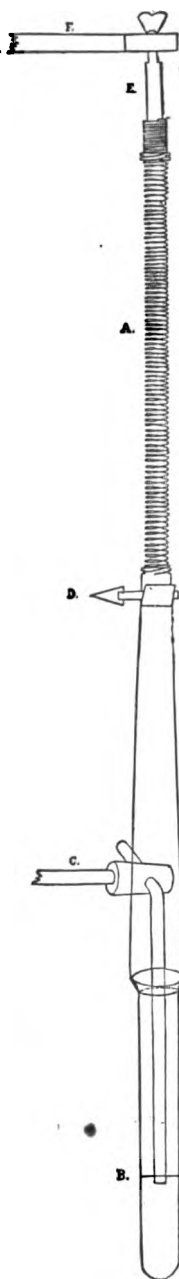
† Wiener medicinische Jahrbücher, 1876, IV.

In the plethysmograph here presented, the balance of Von Basch is replaced by a steel spring, the elongation of which, under a given weight of fluid, is equal to the rise of fluid in the receptacle. The accompanying figure shows the construction of the instrument. The steel spring A has the following dimensions:—

Length (unstretched)	95 mm.
Diam. of coil	12 "
Diam. of wire	0.55 "
Number of coils	165

To the lower end of this spring is suspended by two threads a large-sized test-tube, B, into which enters through the bent tube C the fluid coming from the organ, the changing volume of which is to be measured. The length of the steel spring is so chosen, that the entrance of any given quantity of fluid into the test-tube B causes an elongation of the spring equal to the rise of the fluid in the test tube. The vertical portion of the tube C is of the same length as the test-tube, and since its position is such that its lower end is always just below the level of the fluid in that receptacle, the fluid will not only be driven into, but will be withdrawn from, the test-tube in precise conformity with the varying volume of the organ to be measured. A delicate metallic pointer, D, attached to the lower end of the spring A, is brought in contact with smoked paper, covering the surface of a revolving cylinder, and thus records the varying position of the test-tube B, and consequently the changing volume of the organ to be measured.

It is evident that the elongation of the spring under the weight of a given quantity of fluid will be equal to the rise of the fluid in the test-tube only so long as its specific gravity remains constant. If, therefore, the instrument is to be used with fluids of different specific gravities, a special adjustment of the apparatus will be necessary. This is most readily effected by shortening the spring A in proportion to the increase of specific gravity of the fluid used. In order to do this, it is only necessary



to screw the spring higher up on to its support, E. This support consists of a strip of brass fastened to a short pivot, which passes through a hole in a plate attached to the rod F. The width of the strip of brass, except at its lower end, is such that it lies freely within the coil of the spring. At its lower end it has a projection on each side, which give it a width a little greater than the external diameter of the coil. These projections are notched to receive a single coil of the spring, which is thus wholly supported from these notches, the part of the spring above this point being entirely unaffected by the weight of the apparatus below. In order to alter what may be called the "working length" of the spring, it is only necessary to twist the spring A upon the support E. The notches slide round upon the coils, and by thus changing the point of support alter the length of that portion of the spring which is affected by the weight attached to it. In the present apparatus it is found that the shortening of the spring by a single coil adjusts it for a fluid of  $7^{\circ}.48$  additional specific gravity. Thus if blood (of Sp. Gr. = 1055) is the fluid used, as in measuring the varying capacity of the blood-vessels of an organ, the spring has to be shorter by 7.35 coils than in the case of distilled water.

## III.

## BOTANICAL CONTRIBUTIONS.

BY ASA GRAY.

Presented February 12 and May 14, 1879, with later Additions.

1. *Characters of some new Species of Compositæ in the Mexican Collection made by C. C. Parry and Edward Palmer, chiefly in the Province of San Luis Potosi, in 1878.*

**PIQUERIA SERRATA.** Glabra; caule  $1\frac{1}{2}$ –3-pedali e basi perennante ramoso; foliis amplis (3–5-pollicaribus) omnibus oppositis ovato-oblongis acuminatis. grosse argute serratis (dentibus utrinque 12–15) basi in petiolum brevem marginatum subito contractis triplinerviis vel fere trinerviis, nervis lateralibus tenuibus; capitulis corymboso-cymosis trifloris; involucri bracteis ovalibus obsolete trinerviis; acheniis annulo conspicuo deciduo coronatis, callo basilari parum obliquo. — Mountains at Alvarez, thirty miles southeast of the city of San Luis Potosi, Aug., Sept. No. 496. Involucre 2 lines long.

**STEVIA STENOPHYLLA.** Fruticosa, humilis, glabra, glutinosa; foliis omnibus oppositis angustissime linearibus (poll. 2–3 longis lineam latis) integerrimis eveniis, costa haud prominula; ramis floridis gracilimib; capitulis subsessilibus fasciculatis corymbiformi-cymosis; corolla alba; acheniis inter costas scabro-hirtellis; pappi paleis coroniformi-subconcretis muticis vel in pleris 2–3-aristatis. — Rocky hills near San Luis Potosi, blossoming through the year. No. 319. A very distinct species, allied to the narrow-leaved form (*S. angustifolia*, HBK.) of *S. salicifolia*, Cav. Foliage of purplish-green hue, very glutinous. Among the forms of *S. salicifolia* collected was a very dwarf one (no. 326), var. *nana*. The appended note relates to an *Ageratoid* genus, which is not in Palmer and Parry's collection.\*

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\* **OXYLOBUS**, Moçino. *Phania* § *Oxylobus*, DC. Prodr. v. 114. Distinguishing this from true *Phania*, Bentham and Hooker append *P. arbutifolia*, DC., to *Ageratum*, following Kunth, and leave the *P. trinervia*, DC., uncertain. I propose to

**EUPATORIUM TURBINATUM.** Puberulum; caule herbaceo stricto bipedali; foliis subsessilibus ovato-lanceolatis acuminatis inæqualiter argute serratis basi trinervatis supra scabridis subtus cinereo-tomentulosus, venis laxè reticulatis; cymulis oligocephalis ramos fastigiatos terminantibus; involucri 30-40-floro obconico multiseriali, bracteis gradatim imbricatis rigidulis 2-3-striatis lanceolatis acuminatis, intimis linearibus disco adæquantibus; corollis albis? angustissimis breviter 5-dentatis; acheniis præsertim ad angulos hirsutulis. — In a mountain ravine between San Luis Potosi and Tampico, Palmer. No. 1075. A somewhat peculiar species of the *Imbricata* division, but not of the *Cylindrocephala* or *Osmia* section. Heads half an inch long.\*

**EUPATORIUM RHODOCHLAMYDEUM.** *E. malvæfolio* aliquantum simile; caule herbaceo ultraorgyali; ramis pube ferruginea et glandulosa tomentellis; foliis oppositis, caulinis amplis late hastato-deltoides acuminatis inæqualiter dentatis longe petiolatis, ramealibus ovato-

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reinstate the genus, and to add *Ageratum glanduliferum*, Schultz Bip. in Liebm. Mex. collection, which appears like the rest to be shrubby. All three species, or at least the two of which specimens are in hand, agree with each other, and differ from *Ageratum* in these characters: Involucri pauci-pluriflorum; phyllis 1-2-seriatis æqualibus. Corolla fauce e tubo gracili subito ampliata, lobis angustis sat longis acutis. Achenia basi stipitato-attenuata. Pappi paleæ breves fimbriato-laciniatæ. Frutices vel fruticuli Mexicani.

**O. ARBUTIFOLIUS.** *Ageratum arbutifolium*, HBK. Nov. Gen. & Sp. iv. 149. *Stevia arbutifolia*, Willd. ex Less. in Linnæa, v. 140. *Phania arbutifolia*, DC. Prodr. v. 115.

**O. TRINERVIUS,** Moçino, Ic. Fl. Mex. t. 527. *Phania trinervia*, DC. l. c. Known only by the drawing, recently published by A. DC.

**O. GLANDULIFERUS.** *Ageratum glanduliferum* (at least the  $\beta$ . *albiflorum*) Schultz Bip. in coll. Liebm.

**AGERATUM MICROPHYLLUM,** Schultz Bip. in Seem. Bot. Herald, 298, from the Sierra Madre in Northern Mexico, is a remarkable fruticulose species, with racemose heads (which are much more than five-flowered) and the involucre imbricated in the manner of *Hofmeisteria*. It is the plant of which Benth. in Gen. Plantarum makes a second species of *Decachæta*, and which Hemsley is figuring as such. From my specimen it is not quite manifest that the anthers are inappendiculate; and the pappus is very unlike that of *Decachæta Hænkeana*.

\* **EUPATORIUM ADENOSPERMUM,** Schultz Bip. in Seem. Bot. Herald, 299, Var. **PLEIANTHUM.** Capitulis in ramis gracilioribus paucis 20-floris; foliis plerisque oppositis rigidioribus ovatis subcordatis dentibus multo majoribus paucisque serratis. — I have this from Seemann's northwestern Mexican collection along with the form which Schultz described, and cannot doubt it belongs to the same species, which is a very strongly marked one, but needs to be characterized anew.

**EUPATORIUM LONGIPES.** *Bulbostylis pedunculosa*, DC. The latter specific name is preoccupied in *Eupatorium* by a South American species. (No. 360.)

*lanceolatis*; cymis corymbiformibus polycephalis laxis; pedicellis filiformibus; capitulis 25–30-floris; involucri campanulato (lin. 4 longo) pluriseriali, bracteis gradatim imbricatis papyraceis 3–5-nervatis obtusissimis præter extimas brevissimas glanduloso-pubescentes glaberrimis roseo-tinctis ovalibus oblongis, intimis linearibus; corollis stylisque elongatis rubellis; acheniis glabriusculis; pappo albo deciduo. — On the eastern side of the mountains east of San Luis Potosi. No. 1082. A striking species; the tall and branching stems forming large clumps, and the very numerous rose-colored heads ornamental. The receptacle is plane and glabrous. Leaves copiously resinoso-atomiferous beneath and puberulent; the upper cauline five or more inches in length.

*EUPATORIUM MENDEZII*, DC.? Var. *ACUMINATISSIMUM*. Pubescentius tomentella; foliis plerumque sensim caudato-acuminatis; acheniis secus costas hispidulis. — No. 340. The very numerous and paniculate heads are only 3 lines long, shorter than those of *E. stillingiaefolium*, the flowers smaller, and the corolla white. I have no specimens of *E. Mendezii*; and this is perhaps a wholly distinct species.

*EUPATORIUM SCORODONIODES*. *Eximbricata*, fruticosum, canescens; foliis oppositis deltoideo-subcordatis nunc cordatis crenatis petiolatis basi 3–5-nerviis subtus rugoso-venosis albido-tomentosis supra puberulo-velutinis (pollicaribus, superioribus semipollicaribus); cymis corymbiformibus oligocephalis; capitulis omnibus pedicellatis; involucri 20–40-floro subuniseriali e bracteis lanceolato-linearibus acutis; pappo corollam albam subæquante. — Rocky hills near San Luis Potosi, May and June. No. 336. Heads 5 and the involucre 3 lines long. Corolla with rather large ovate-lanceolate lobes. A branching shrub, only a foot or two high; in two forms, one with small leaves, the other with larger and more flaccid leaves, perhaps growing in shade.

*EUPATORIUM PORPHYRANTHEMUM*. *Subimbricata*, glabellum; caule herbaceo laxo 1–2-pedali; foliis oppositis longe petiolatis membranaceis rhombico-ovato-lanceolatis seu e basi lato-cuneata ovato-acuminatis grosse serratis triplinerviis; cymulis oligocephalis in pedunculo nudo laxè corymboso-cymosis; capitulis omnibus pedicellatis 20-floris; involucri campanulato (lin. 3 longo) gradatim laxè imbricato triseriali glabro viridulo, bracteis omnibus obtusis binerviis, extimis paucis brevibus ovalibus, cæteris oblongo-linearibus, intimis apice sæpius purpuratis; corollis roseo-purpureis; acheniis ad costas hirtellis. — Between San Luis Potosi and Tampico, at the eastern base of the mountains, Palmer. No. 1083. Belongs to the group of *E. pycnocephalum*, Less., the *E. Schiedeianum* of Schrader, &c. Receptacle plane.

**EUPATORIUM HYSSOPINUM.** *Eximbricata*, subglabrum; caulibus herbaceis (pedalibus) e basi suffruticosa usque ad cymam corymbiformem æqualiter foliosissimis; foliis oppositis parvulis (lin. 6–10 longis) lanceolatis utrinque acutiusculis integerrimis uninerviis subsessilibus; capitulis pluribus pedicellatis; involucrio biseriali e bracteis 14 oblongo-linearibus villosis-ciliatis floribus 18–24 dimidio brevioribus; pappo corollam (lin. 3 longam) subæquante. — Mountains near San Luis. No. 337. In habit the plant may be likened to *Pycnanthemum lanceolatum*. Lobes of the corolla rather long, lanceolate.

**EUPATORIUM AMPLIFOLIUM.** *Eximbricata*, *E. Pazcuarensi* et *E. grandidentato*, DC. subsimile; caule glabro orgyali; foliis subglabris oppositis et alternis ovatis acuminatis dentato-serratis longius petiolatis, summis (3-pollicaribus) basi subcuneatis, inferioribus (4–6-pollicaribus) subcordatis; capitulis paniculato-cymosis 12-floris; pedicellis cinereo-pubescentibus; involucrio glabriusculo; pappo deciduo corolla alba angusta prorsus glabra brevior. — In forest, on high mountains southeast of San Luis Potosi, Sept. No. 334. The heads are larger and fewer-flowered than those of Mexican specimens from Schultz named *E. Pazcuarensis*, and from the very similar *E. grandidentatum*, DC.; also the corolla lacks the scattered long hairs which I find in the above-mentioned species.

**EUPATORIUM ESPINOSARUM.** *Eximbricata*, viscosum, fere glabrum; caulibus fruticosis ramosis bipedalibus; ramis foliosis cyma subsimplici sessili corymbiformi terminatis; foliis oppositis submembranaceis (cum petiolo sat longo 1–2-pollicaribus) lucidulis glutinosis ovatis et ovato-lanceolatis serratis nunc inciso-dentatis triplinerviis; capitulis (lin. 3–4 longis) breviter pedicellatis confertis 12–17-floris; involucrio fructifero acheniis secus costas hirtellis parum longiore e bracteis 9–10 lineari-oblongis obtusis subcrassis 1–3-nervatis; corolla alba angusta, lobis brevibus ovatis pappum paullo superantibus. — In oak-thickets on the sides of a mountain near San Luis. No. 333. A well-marked species of the group to which *E. Berlandieri* belongs; the white-flowered heads abundant and handsome. Dedicated to the brothers Don Antonio and Don Manuel Espinosa y Cervantes, who hospitably promoted the formation of this collection. Don Antonio, a civil engineer, was the Secretary of the United States and Mexican Boundary Commission.

**E. ESPINOSARUM, var. AMBIGUUM.** Parum glutinosum; caulibus floridis strictis fere herbaceis apice paniculato-cymosis; foliis haud lucidis. No. 344. Apparently not distinct from the preceding species.



BARROETEA, Nov. Gen. *Eupatorinearum*.

Involucrum (15–25-florum) floresque *Kuhnia* et *Brickellia*. Achenia oblonga, compressa, binervia, nervis marginalibus tenuibus ciliolatis, lateribus nec costatis nec striatis, callo basilari magno. Pappus simplex, e setis capillaribus uniserialibus pauciusculis (12–20) æqualibus rigidulis e disco epigyno achenio angustiore. — Plantæ Mexicanæ, graciles; foliis plerisque oppositis ovatis petiolatis dentatis, dentibus sæpe aristatis, pube minuta.

BARROETEA SETOSA. Herbacea, ramosissima; radice ut videtur perenni; foliis membranaceis grosse argute serratis vel duplicatodentatis, dentibus fere omnibus promissae aristatis; capitulis in axillis brevi-pedunculatis folio fulcrante plerumque superatis; achenio ad margines hirto-ciliato; pappi setis crebre serrulato-scabris. — Mountains southeast of the city of San Luis Potosi. No. 353.

BARROETEA SUBULIGERA. Fruticulosa, corymboso-ramosa; foliis crenato-serratis, acumine sæpe dentibusque posticis subulato-mucronatis; capitulis longe pedunculatis corymbosis (char. præced. e Schauer); involucri bracteis magis attenuatis; achenii marginibus ciliolatis; pappi setis tenuissime scabris. — *Bulbostylis subuligera*, S. Schauer in *Linnaea*, xix. 718. Zimapan, Mexico, Aschenborn.

It was evident from the published description of Schauer's *Bulbostylis subuligera*, with its flat achenia, that it was a congener of the plant scantily collected by Parry and Palmer, and distributed as No. 353. I am indebted to Prof. Eichler of Berlin for the communication of a capitulum of Aschenborn's plant, which confirms the determination. These two plants want the technical character both of the *Agerateæ* and of the *Adenostyleæ*, as arranged by Bentham (which subtribes should therefore be merged and distributed into mere sections), and they form a well-defined genus, which, at the instigation of the collectors of one species, I dedicate to their good friend, Professor Barroeta, of the School of Mines at San Luis Potosi, a competent naturalist, who has devoted considerable attention to the botany of the province.

BRICKELLIA HYMENOCHLÆNA. Herbacea, minute puberula; caule simplici pedali 10–14-phyllo apice nudo corymboso-oligocephalo; foliis oppositis ovatis vel deltoideo-oblongis nunc subcordatis obtusis crenato-serratis vel integriusculis petiolatis; capitulis pedicellatis (ultrasemipollicaribus); involucri lato-campanulato circa 30-floro pauciseriali; bracteis plerisque tenuiter membranaceis scariosisque purpureo tinctis ovalibus vel spathulatis acuminatis cum mucrone gracili, extimis paucis laxis lanceolato-subulatis parum herbaceis;

acheniis pubescentibus. — Foot-hills of the mountains near San Luis, May or June. The simple stems, from six to eighteen inches high, rise from a firm and knobby caudex. No. 349.

**BRICKELLIA SQUAMULOSA.** *B. spinulosa* affinis, fruticosa, pube minutissima tomentulosa cinerea; ramis gracilibus elongatis fastigiatim ramulosis; foliis (caulina desunt) ramulorum minimis (vix lineam longis) linearibus seu oblongis squamiformibus plerisque tetrasticho-imbricatis; capitulis ramulos terminantibus; involucrio clavato-turbinato 10–12-floro e bracteis pluriserialibus gradatim imbricatis extus canescentibus obsolete striatis acutiusculis, intimis lineari-lanceolatis, extimis brevibus ovatis; acheniis glaberrimis; pappo rariter hirtello-scabro. — Abundant in gravelly soil, near San Luis Potosi, forming large clumps, two or three feet high, May to July. No. 356. Head half an inch long, including the outermost series of bracts, which pass into the squamaceous leaves.

**BRICKELLIA THYRSIFLORA.** Herbacea e basi frutescente puberula, subviscosa; caule (1–3-pedali) ramosissimo apice pyramidato-ramoso ramisque floridis polycephalis foliosissimis; foliis alternis lato-lanceolatis basi apiceque acutis vel acuminatis vix petiolatis integerrimis scabridis, venulis utrinque reticulatis; capitulis thyrsideo-paniculatis numerosis breviter pedicellatis erectis (semipollicaribus); involucrio cylindraceo 10–14-floro e bracteis gradatim imbricatis extus glanduloso-puberulis, omnibus obtusissimis vel mucronulato-acutis, intimis lineari-oblongis, extimis late ovalibus; acheniis ad costas parce hirtellis; pappi setis supra medium barbellulatis. — Mountains southeast of San Luis Potosi, Aug. No. 362.

**B. PALMERI.** Herbacea, scabrido-puberula; caule ramoso pedali; foliis (superioribus) subalternis ovatis vel deltoideis paucidentatis scabris rigidulis subtus reticulatis breviter petiolatis parvulis; capitulis sparsis in pedunculo gracili (ultrasemipollicari) erectiusculis; involucrio campanulato 12–15-floro; bracteis interioribus lineari-lanceolatis exquisite acuminatis glabris (lin. 5 longis), exterioribus multo brevioribus latioribus subviscoso-puberis acutis; acheniis pubescentibus. — Near San Luis Potosi. No. 354. This should be compared with *B. (Bulbostylis, DC.) reticulata*, which would be a good name for it; but the leaves of our plant are coarsely toothed, and the heads can hardly be said to be racemose, nor the pubescence velvety. The lower leaves may be cordate.\*

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\* **BRICKELLIA SEEMANNI.** Ramis herbaceis simplicibus puberulis, apice nudo capitula 6–8 unilateraliter spicata nutantia confertim gerente; pedicellis brevissimis bractea parva suffultis; involucrio circiter 25-floro, bracteis tenuiter

**BRICKELLIA** **PARRYI.** *B. Galeottii* affinis, inter *B. Cavanillesii* et *B. veronicæfoliam* collocanda, frutescens, 1–3-pedalis, canescenti-tomentulosa, haud glandulosa; ramis virgatis; foliis plerisque alternis cordatis vel subcordato-ovatis obtusis crenato-serratis supra scaberulis subtus tomentosis reticulatis (semi-sesquipollicari et petiolo lin. 2–5 longo); capitulis conferte paniculatis suberectis semipollicaribus pedicello subæquilongis; involucri campanulato 15–20-floro e bracteis circiter 20 omnibus obtusis vel obtusiusculis, intimis linearibus glabris, exterioribus ovatis oblongisque dorso puberis. — High mountains southeast of San Luis, Aug. No. 363. The heads are intermediate in size and in the involucre between *B. Cavanillesii* and *B. veronicæfolia*. I possess no specimen of *B. Galeottii* (which Schultz Bip. took to be the *Rosalesia glandulosa* of Llave and Lexarsa), with which this should be critically compared. The pubescence is that of *B. tomentella* and of the more downy forms of *B. Cavanillesii*.

**GUTIERREZIA** **BERLANDIERI.** *G. eriocarpæ* facie, magis paniculata; capitulis sparsis paullo minoribus; involucri (lin. 2 longo) subcampanulato e bracteis oblongis; ligulis 9–15 sat longis; acheniis sericeo-pubescentibus; pappo (radii et disci) brevissimo (pilos achenii parum superante) multipaleolato; receptaculo parum pubescente. — Near San Luis Potosi, Berlandier (No. 1298). and in Tamaulipas (No. 926, 2316); near Saltillo, Gregg (No. 538); No. 370 and 367 of Parry and Palmer's collection from San Luis, where it abounds in waste grounds and is used for brooms. A species which has long been left doubtful and undescribed; well marked by its pappus of 12 to 18 minute short paleæ, which are slightly united at base, forming a crown which barely equals or at length moderately exceeds the soft pubescence of the achenium.

**XANTHOCEPHALUM** **SERICOCARPUM.** E basi vix frutescente? 1–2-pedale; ramis gracilibus fastigiatis apice monocephalis; foliis (ramorum) angusto-linearibus integerrimis, inferioribus hirtello-ciliolatis; capitulo subgloboso (lin. 3 longo) multifloro; ligulis 10 oblongis (sesquilineam longis); receptaculo demum conico; acheniis pl. m. tetra-

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chartaceis 3–4-seriatim imbricatis, omnibus mucrone gracili attenuato-acuminatis, extimis ovatis, intimis lineari-lanceolatis (semipollicaribus et ultra); foliis alternis breviter petiolatis ovatis acutiusculis subserratis subcoriaceis grosse reticulatis (1–2-pollicaribus) utrinque viridibus supra hispidulo-scaberimis subtus ad venas venulasque hispidulo-scabris. — N. W. Mexico, in the Sierra Madre? Seemann. Not in the Botany of the Herald; for the *B. pendula* there enumerated is said to have monocephalous branchlets. In the form and venation of the leaves it is not unlike *B. Palmeri*.

gono-obpyramidatis pube densa sericea incanis apice truncatis disco cartilagineo integro parum cupulato coronatis. — Near San Luis Potosi, where it is common on gravelly hills, July. No. 369.

**BIGELOVIA OPPOSITIFOLIA.** *Chrysolhamnopsis*, anomala, frutex ramosissimus, pumilus, glabellus; foliis oppositis! petiolatis crassocoriaceis lanceolato-oblongis cuspidato-acutis rariter acute dentatis trinervatis et obsolete venosis punctatis glutinosis (semipollicaribus); capitulis subsolitariis ramos ramulosque breves foliosos terminantibus intra folia sessilibus; involucri 20–25-floro e bracteis æquilongis chartaceo-coriaceis paucistriatis acutis 2–3-seriatis, exterioribus lato-lanceolatis, intimis linearibus; corollis angustis breviter 5-dentatis; styli ramis appendice filiformi parte stigmatosa æquilata duplo longiori; acheniis angustis 4–5-angulatis puberulis pappo rigidulo uniseriali parum brevioribus. — Rocky hills near San Luis Potosi, May. No. 359. Head half an inch long. This must needs be referred to *Bigelevia*, but it is remarkable for the opposite leaves and the equal bracts of the involucre.

**ASTER POTOSINUS.** *Orthomeris*, totus glaber; caulibus gracilibus e caudice repente 8–18-pollicaribus; foliis omnibus gramineis linearibus integerrimis, imis (2–5 pollicaribus lin. 2 latis) basi attenuatis; caulibus plerisque e basi latiori semiamplexicauli subulato-attenuatis; capitulis paucis; involucri 3–4-seriatis bracteis gradatim imbricatis adpressis lanceolatis acutis margine albido-scariosis dorso viridibus; ligulis ut videtur albis; styli fl. herm. ramis brevibus latis, appendice ovato-subulata parte stigmatosa parum brevior; ovariis parce pubescentibus. — Along brooks in the mountains of San Luis Potosi. No. 384. Heads smaller than those of *A. pauciflorus* (*A. caricifolius*, HBK.); the bracts of the involucre imbricated in the manner of *A. Sonora*, &c.

**ASTER (MACHÆRANTHERA) GYMNOCEPHALUS.** *Aplopappus gymnocephalus*, DC. Prodr. v. 346. *Machæranthera setigera*, Nees in Linnaea, xix. 722? The rays are bright violet-purple. (See Plantæ Wrightianæ, i. 97.) No. 379.

**ERIGERON PALMERI.** *Euerigeron*, glabellum; caule e radice perenni erecto gracili (1–2-pedale) aut aphylo monocephalo aut inferne foliato nunc sat foliato, pedunculis 2–3 elongatis monocephalis; foliis integerrimis vel grosse pauciserratis, radicalibus spatulato-oblongis obtusis crassiusculis (4–5-pollicaribus) in petiolum gracilem sensim attenuatis, caulinis (raro pollicaribus) oblongo-lanceolatis sessilibus; involucri e bracteis lineari-lanceolatis acutis vel acuminate æquilongis parum pubescentibus; ligulis 80–90 (semipollicaribus albis?); pappo

simplici. — Mountains of Alvarez, southeast of San Luis, August. No. 395. In one form the large head is raised on a scape two feet high, which bears only a few minute subulate bracts and one or two small leaves at base; the glabrous radical leaves ample and smooth; another has a several-leaved stem which is somewhat branched above, the peduncles 3 or 4 inches long; and there are intermediate forms.

**BACCHARIS SEEMANNI.** Glabra, sesquipedalis; caulibus herbaceis rigidis junceis striato-sulcatis pedalibus simpliciusculis e basi lignescente monocephalis vel ramis paucis strictis capitulo pedunculato terminatis; foliis sparsis linearibus basi attenuatis rigidulis acutiusculis (majoribus sesquipollicaribus lin. 1-2 latis), costa inconspicua; involucrio turbinate vel oblongo-campanulato, bracteis pluriseriatim imbricatis acutis dorso viridibus marginibus anguste scariosis. — *B. Wrightii*, Schultz Bip. in Seem. Bot. Herald, 303, non Gray. San Luis Potosi, near streams, June. No. 411. Both sexes are in the collection; from that of Seemann we have only the female. The species is completely different from *B. Wrightii*, has a narrower and fewer-flowered involucre, the bracts of which are greener, more rigid, broader, and merely acute; and the habit is more junciform.

**BACCHARIS RAMIFLORA.** Frutescens, 1-3-pedalis, fere glabra, glutinosa, foliosa; ramis sulcato-striatis; foliis lanceolatis seu linearispatulatis basi attenuatis subpetiolatis subtripplinerviis acutis integerrimis nunc dentibus 1-2 instructis, majoribus tripollicaribus, ramulorum parvis, ultimis bracteiformibus capitula racemoso-paniculata ramulos terminantia fulcrantibus; involucrio campanulato (lin. 2-3 longo), bracteis nudis lanceolatis acutiusculis vel fœm. obtusiusculis. — Gravelly hills near streams, San Luis Potosi, June. No. 404, 412.

Var. **SQUARRULOSA.** Ramulis floridis ericoideo-foliosissimis; foliis (lin. 2-3 longis) recurvo-patentibus. With the other form. No. 408.

**BACCHARIS POTOSINA.** Fruticulosa, glabra; ramis junciformibus striato-angulatis; foliis angusto-linearibus acutis inferne attenuatis sessilibus subuninerviis integerrimis (majoribus sesquipollicaribus lineam vel semilineam latis); capitulis parvis (masculis lin. 2 fœmineis lin. 3 longis) laxè paniculatis omnibus pedunculatis circiter 20-floris; involucrio masculo campanulato e bracteis pauciserialibus lanceolatis acutis subscariosis, fœmineo fere oblongo e bracteis pluriserialibus obtusis. — Borders of streams in the mountains. No. 410. Plants apparently only a foot or two high, with somewhat the habit of *B. sergiloides*, but with longer and slender leaves, more pedunculate heads, narrower involucreal bracts, &c. It should be compared with

De Candolle's *B. linifolia*, which is said to have a terete simple stem, scabrous-serrulate leaves, and corymbose heads.

**GNAPHALIUM CONCINNUM.** *Rhodognaphalium* (Schultz Bip.); caulibus subherbaceis e basi parum lignescente pedalis; foliis oblongis obtusis fere planis mollibus (lin. 6-9 longis 2-3 latis) supra viridulis floccoso-pubescentibus subtus dense cano-lanatis; cyma corymbiformi fere aphylo; capitulis floribusque fere *G. Seemannii*; involucri bracteis exterioribus appendice lactea oblonga obtusissima radiato-patente terminatis. — In the highest mountains southeast of San Luis, No. 423. This is the handsomest species of that peculiar Mexican group, founded by Schultz on his *G. Seemannii* and *G. rhodanthum*, to which he should have added *G. lavandulæfolium*, DC., and which Benthams, in the *Genera Plantarum*, refers to *Chionolæna*, DC. They are andine species, with very leafy stems, the older leaves below reflexed and marcescent, the living ones widely spreading; the involucri of the heads with showy and radiant petaloid tips; the flowers purple or rose-color. In *G. Seemannii* (which Hemsley has recently redescribed under the name of *Chionolæna corymbosa*), and in the present species, the pappus of the hermaphrodite flowers consists of conspicuously clavellate-tipped bristles; in *G. rhodanthum* and *G. lavandulæfolium* they are only slightly so. I do not find that they are united at base, certainly they are not "basi in cupulam concretis," and for the most part they seem to fall away singly. The style of these flowers is bifid at the apex in all but *G. lavandulæfolium*, and not always quite entire in that. The ovary is ovuliferous, but generally it appears to be sterile. The involucrial bracts in *G. rhodanthum* are less radiant than in the two more northern species. I have not seen the Brazilian *Chionolæna*, but, upon the above data, these Mexican species can hardly belong to that genus, nor be well separated from *Gnaphalium*. The stem of *G. concinnum* seems to be nearly herbaceous, but enduring, being in some specimens continued by successive growths beyond the cymes of one or two former seasons, leaving these deeply lateral.

**LINDHEIMERA MEXICANA.** Pumila, a basi ipsa florens; foliis lyrato-pinnatifidis longius petiolatis, lobis inciso-dentatis; ligulis 8-10 oblongis grosse 2-3-dentatis; acheniis lævibus ala conspicua scariosa sinuato-incisa sursum latiore cinctis a paleis contiguis liberis; dentibus lateralibus pappi obscuris alæ accretis, interno majusculo; stylo fl. masc. apice bifido. — Between the city of Mexico and San Luis; station not specified. No. 447. The genera related to *Silphium* are not very strongly marked; and the reference of the present plant to

*Lindheimera* calls for some modification of the generic character. Its affinity with this genus is shown in the peculiar porrect internal tooth or process which surmounts the carina or costa of the inner face of the akene (a character which is omitted from Bentham and Hooker's *Genera Plantarum*). The peculiar scarious wing appears to be that of *Schizoptera* (which is said to have a slender tube to the ligules and a different habit). The habit of this plant is that of *Chrysogonum Virginianum*, but with the lyrate leaves of *Berlandiera lyrata*. It accords with *Silphium* in that neither the adjacent paleæ (which are very slender) nor the subtending involucrel bract adhere to and fall away with the achenium. The root is perhaps perennial.

**PHILACTIS LONGIPES.** Scabrido-pubescent; foliis brevissime petiolatis ovatis parce inæqualiter dentatis, summis lanceolatis; capitulo in pedunculo terminali longissimo solitario; receptaculo mox columnari ligulas oblongas (semipollicares) longius superante; acheniis (immaturis) omnibus complanatis glaberrimis (faciebus nec costatis nec angulatis), radii obcompressis marginibus acutis apice emarginatis vel retusis calvis, disci parum angustioribus crassioribus nunc calvis nunc dentibus obtusis parvis 2 (ex marginibus) vel 4 (accessoriis minimis alternantibus) instructis. — In valleys along the foot-hills of the mountains near San Luis Potosi, July. No. 465. The original *Philactis* is very little known, the drawing communicated by Schrader to the elder DeCandolle remaining unpublished. But this is without much doubt a second species of the genus, with the awns (answering to the pappus) obsolete, yet in some cases indicated by soft teeth or denticulations, with foliage perhaps not unlike that of *P. zinnioides* (the leaves at most an inch long), but with a naked peduncle from two to fourteen inches long. The ligule is sessile on the broad and flat ovary. The latter may become trigonal at maturity, but it shows no facial angle. From the appearance of the style and the ovary it may be expected that the disk-flowers are also fertile. The narrow columnar receptacle attains the length of fully three quarters of an inch.

**ZALUZANIA MOLLISSIMA.** Fruticosa (circiter 3-5-pedalis); foliis oblongo- seu rhombeo-ovatis inferne subito petiolatim angustatis integerrimis vix repandis (poll. 1-2 longis) supra ramisque tenuiter floccoso-lanatis subtus tomento denso albo permolli incanis; pedunculis brevibus 1-3-cephalis; involucri bracteis oblongis obtusissimis; ligulis 7-8 obovatis subintegerrimis pro capitulo magnis (semipollicaribus); acheniis radii pappo tenuiter squamellato nunc ex angulo interno aristellato. — Gravelly ridges south and east of San Luis, Sept. No. 446.

**GYMNOLOMYA GREGGII.** Fruticosa, tomento brevissimo incana; foliis plerisque oppositis ovatis obtusis integerrimis basi cuneatis in petiolum brevem attenuatis subtus argenteis supra pube minuta tantum cinereis (majoribus pollicaribus); capitulis ramulos corymbiformes terminantibus; involucri bracteis 3-serialibus gradatim imbricatis oblongis acutiusculis siccis canescentibus; ligulis 8-10 oblongis; corollis disci basi ampliatis apicem ovarii glabri calyptratim tegentibus. — Northern part of Mexico, Dr. Gregg, 1848-49. No. 382 of the present collection. The flowers of the ray are sterile, but there is sometimes a rudimentary style. There is, as in most of the species, no trace of a pappus.

**ZEXMENIA GNAPHALIOIDES.** Floccoso-lanata, ramosa; ramis virgatis elongatis e basi vel caule lignescente apice longe nudo monocephalis; foliis parvis (lin. 6-9 longis) deltoideo-ovatis vel cordato lanceolatis breviter petiolatis integerrimis margine demum revolutis supra pube brevi sericeo-hispidula cinereis subtus tomento pannoso incanis; capitulo subgloboso (semipollicem lato); involucri bracteis foliaceis fulcrato et e bracteis propriis coriaceis oblongis obtusissimis adpressis gradatim pauciseriatim imbricatis, intimis linearibus papyraceis; ligulis oblongis; acheniis hispidulis nunc exalatis nunc ala crassa cinctis; pappo inter aristas subulatas achenium æquantibus utrinque 3-4-squamellato, squamellis linearibus vel subulatis, majoribus aristis dimidio brevioribus. — Collected by Dr. Palmer on the journey between San Luis and Tampico, only the flowering branches of a most remarkable species, nearly past blossoming. No. 1106.

**PERYMENIUM PARVIFOLIUM.** Suffruticosum, pube adpressa scabrida subcinereum; caulibus gracillimis laxis brachiato-ramosis apice longe nudo subumbellatim oligocephalis; pedicellis filiformibus; foliis fere concoloribus oblongo-lanceolatis utrinque obtusis leviter trinerviis integerrimis ( $\frac{1}{2}$ -1 poll. longis) brevissime petiolatis; involucri (lin. 2 longo) pauciseriali; ligulis 7-9 oblongis; paleolis pappi 2 (in radio 3) elongatis aristiformibus cæteris fere setiformibus brevibus, omnibus hispidis. — On the edge of ravines near San Luis, in dense clumps, August. No. 475.

**PERYMENIUM TENELLUM.** Herbaceum, hispidulum; caulibus diffusis spithamæis; foliis fere concoloribus oblongis ovalibusve obtusis basi acutiusculis brevi-petiolaris pauci-dentatis triplinerviis paucivenosis parvis (lin. 5-9 longis); pedunculis 1-3 ex apice caulis elongatis filiformibus monocephalis; involucri biseriali (lin. 3 longo), bracteis exterioribus 5-6 herbaceis oblongis interiores membranaceas angustiores paullo superantibus; paleis receptaculi subulato-cuspi-



dati; pappo ex arista unica elongata rariter denticulata et setis tenuibus brevibus. — Old fields, near the city of San Luis Potosi, August. No. 450. Intermediate in character between *Perymenium* and *Melanthera*, it might be placed among the radiate yellow-flowered species of the latter; but the almost mature heads are not globular, and the involucre remains erect. Only the simpler and more herbaceous involucre distinguishes the plant from true *Perymenium*.

**ENCELIA MICROPHYLLA.** Fruticulosa (pedalis), scabro-puberula; ramis floridis (spithamæis) apice nudo pedunculiformi monocephalis; foliis alternis (semipollicaribus) viridibus coriaceis ovato- seu oblongo-lanceolatis cuspidato-acuminatis basi acutis vix petiolatis integerrimis penninerviis concoloribus inter venas primarias minutim reticulatis; involucri bracteis lanceolatis; ligulis 6-7; acheniis villosissimis exalatis obovatis apice parum emarginatis; pappo nullo. — Gravelly hills near Saltillo, August. No. 462.

**HELIANTHELLA MEXICANA.** *H. Parryi* sat similis, gracilior, monocephala, parce hispida; foliis etiam radicalibus (3-pollicaribus lin. 2-3 latis) lineari-lanceolatis obsolete triplinerviis, caulinis pollicaribus; capitulo pro genere parvo; involucre magis folioso; corollis disci atropurpureis; acheniis immaturis faciebus marginibusque villosissimis apice scarioso-bidentatis cum coronula hyalina parva pluripartita. — In the valley of Mexico, July. No. 463. Head barely half the size of that of *Helianthella Parryi*, and apparently erect, not nodding on the apex of the stem.

**VERBESINA SORORIA.** *V. Siegesbeckiæ* sat similis; sed caule aptero; foliis vix petiolatis magis pubescentibus haud triplinerviis; floribus radii styliferis sed sterilibus ligula ampliore; acheniis disci ala lata subincisa marginatis. — Wooded mountain slopes, near San Luis Potosi, August. No. 466. *V. Siegesbeckia* forms an exception to the character "achenia distincte bialata" in the Genera Plantarum; and the distinction between *Verbesina* and *Actinomeris* is failing; for at least two species referred to the latter are frequently provided with a well-formed style to the ray-flowers, yet with the ovary sterile, as in the present plant. The likeness of the latter to *V. (Phæthusia) Siegesbeckia* is striking, notwithstanding the wingless stem and the broadly winged achenia.

**VERBESINA HYPOCRUCA.** *Verbesinaria, Aptera* DC.; caule virgato bipedali e basi suffrutescente cinereo-puberulo apice nudo paniculatim oligocephalo; foliis lanceolato-oblongis (circ. bipollicaribus) penninerviis grosse dentatis basi plerumque angustata integriuscula arcte auriculato-sessilibus supra velutino-puberulis subtus albo-tomentosis,

inferioribus oppositis; pedunculis gracilibus; capitulis (vix semipollicem diametro) subglobosis; involucri bracteis disco dimidio brevioribus; ligulis brevibus 10–12; acheniis glabris tenuiter 2-aristatis basi attenuatis ala scariosa cinctis. — Ravines near San Luis Potosi, July. No. 474.

**CALEA ALBIDA.** *C. rugosæ* (*Calydermati rugoso*, DC.) affinis; ramis hirsutis; foliis lato-ovatis grosse obtuse dentatis supra scabro-hirtellis subtus pubescentibus rugoso-reticulatis; capitulis paucioribus multo majoribus (lin. 4 longis) plerisque pedunculatis 20-floris; floribus aut omnibus hermaphroditis aut uno alterove fœmineo breviligulato; involucri late campanulato, bracteis oblongis obtusis, extimis laxis subherbaceis pubescentibus brevioribus, cæteris membranaceis albidis tenuiter nervosis glabris disco adæquantibus; corollis ut videtur albis; acheniis hirsutissimis basi stipitato-attenuatis; pappo e paleis 10–12 lanceolatis eroso-denticulatis tubo corollæ adæquantibus. — A densely branched suffruticose plant, on gravelly soil near San Luis, August. No. 448. The capitula have the bitter-aromatic odor and taste of hops. The ray when present does not surpass the disk-corollas.

**CALEA (TEPHROCALEA) TOMENTOSA.** Foliis cordatis obtusis integerrimis quintuplinerviis et venosis petiolatis supra tenuiter subtus ramisque dense albido-tomentosis; pedunculis terminalibus monocephalis; capitulo subgloboso; involucri pauciseriali tomentoso disco dimidio brevior, bracteis ovatis subæquilongis; receptaculo conico; pappi paleis 5 lanceolatis acutis achenio dimidio brevioribus. — Collected by Dr. Palmer on the route between San Luis and Tampico. No. 1108. This species has female ray-flowers; but the scanty heads seen are in such condition that their number (evidently few) and the form of the ligule cannot be well ascertained. In aspect unlike any known *Calea*, except the following in Coulter's collection.

**CALEA (TEPHROCALEA) DISCOLOR.** Foliis oblongis mucronatis integerrimis basi vix subcordatis petiolatis penninerviis subtriplinerviis venulosus supra glabris lucidis subtus ramisque tomento minuto (primum flavescente) incanis; pedunculis 1–3-floris; involucri turbinato-campanulato glabro pluriseriali disco subdimidio brevior, bracteis subulato-lanceolatis; receptaculo angusto conico; ligulis 8–10 (lin. 4–5 longis) oblongis 5-nervatis; pappi paleis 4–5 parvis subulatis. — No. 351 of Coulter's Mexican collection, distributed from the herbarium of Trinity College, Dublin. The flowers are yellow; the larger leaves 3 or 4 inches long.

**TRIDAX PALMERI.** Hirsutulo-puberula; caule erecto bipedali ramoso; foliis (superioribus sæpe alternis) pinnatifido-incisis vel 3–5-

partitis summisve integrisculis; involucri gradatim imbricato 3-4-seriali, bracteis subherbaceis oblongis obtusissimis adpressis, exterioribus cinereo-puberulis; ligulis albis demum roseis dilatatis fere integerrimis (sine lobulis internis); corollis disci viridescenti-flavis; pappi paleis linearibus fimbriato-plumosis tubo corollæ vix adæquantibus achenio dimidio brevioribus. — On rocky bluffs at Alvarez, thirty miles south-east of San Luis, at the elevation of 8,000 feet. No. 489 with broader leaves, 490 and 482½ with narrow leaves. A handsome species; the naked flowering branches somewhat paniculate; heads half an inch high, and the few but large and showy ligules half an inch long on a rather slender tube, their width at the almost truncate apex nearly equalling the length.

TRIDAX (PTILOSTEPHIUM) TRIFIDA, var. ALBORADIATA. Radio albo; foliis latioribus 3-5-fidis, lobis nunc laciniatis. — Gravelly slopes near San Luis, July, August. No. 511. This species includes *Ptilostephium coronopifolium* as well as *P. trifidum* of DeCandolle's Prodrômus, not *P. coronopifolium*, HBK., which, as the figure shows, has the pappus of plumose aristæ in the manner of *T. procumbens*. No. 508 of the present collection is, without much doubt, the true *T. coronopifolia*; but its ray-flowers are properly ligulate and female. Nearly related to it is *T. balbisioides* (*Ptilostephium*, Spreng., *Galin-soga*, HBK., *Sogalgina*, Cass.), if we may rightly refer Parry and Palmer's No. 509 to that species; but the ligule in the specimen is three-cleft instead of entire and reniform.

TRIDAX CANDIDISSIMA. Tomento albo undique lanata; ramis brevibus adsurgentibus crebre foliatis pedunculo nudo scapiformi superatis; foliis linearibus (teretibus?) obtusis sessilibus; capitulo (an semper?) homogamo; involucri sat imbricato; pappo modo *T. procumbentis* plumoso, aristis majoribus corollis flavis parum brevioribus. — On loose ashy soil near Angostura, one hundred miles east of San Luis, coll. by Dr. Palmer, March, 1879. No. 510.

#### EUTETRAS, Nov. Gen. *Helenioidearum*.

Capitulum heterogamum, radiatum, multiflorum; floribus radii 9-12 fœmineis. Involucrum campanulatum, biseriale; bracteis æqualibus disci brevioribus, exterioribus (circa 10) subherbaceis lineari-oblongis substriatis, interioribus siccioribus, omnibus fere planis. Receptaculum convexum, nudum. Ligulæ breviusculæ, oblongæ, apice tridentatæ; corollæ disci ultra tubum proprium brevem angustum cylindrææ, apice 4-dentatæ. Antheræ 4, basi sagittatæ, apice appen-

dice obtusa auctæ. Styli rami fl. herm. appendice sublineari obtusa hirtello-pubera superati. Achenia oblongo-linearia, tetragona, fere glabra, angulis prominulis. Pappus duplex, e paleis 4 brevibus latis truncatis enerviis apice erosis, cum aristis totidem alternantibus setiformibus sursum clavellatis barbellulatis corollam disci subæquantibus. — Fruticulus; capitulis parvulis brevi-pedunculatis; floribus albo-roseis; foliis parvis subalternis cinereo-pubescentibus deltoideo-ovatis dentatis petiolatis.

EUTETRAS PALMERI. — Same station as the preceding, collected by Dr. Palmer, very sparingly. No. 520½. The genus to be placed near *Laphamia* and *Perityle*, of which it has the habit; but with very different achenia and pappus, in these respects more like *Baeria*, section *Dichæta*.

BAHIA ANTHEMOIDES. *Achyropappus anthemoides*, HBK., Nov. Gen. & Spec. iv. 257, t. 390, in which (as DeCandolle states) the "radio albo" is probably a mistake, and the pentaphyllous involucre probably a minimum number. In our plant the involucre is 10-phyllous; the paleæ of the pappus dilated-obovate and nerveless with a narrowed thickened base. The distinctions between *Bahia* and *Schkuhria* have to be determined anew, and *Achyropappus* must fall into the former. No. 494.

TAGETES PARRYI. Elata, ramosissima; ramis gracilibus foliosis capitulo solitario longiuscule pedunculato terminatis cum foliis pinnatis tomentoso-puberulis; foliolis paucijugis subsessilibus ovalibus oblongisve (circiter semipollicem longis) obtusissimis argute dentatis (dentibus acuminatis), additis paucis cauli proximis depauperatis pl. m. setiferis; pedunculo sub capitulo clavato fistuloso; involucre campanulato 8-dentato (semipollicari); ligulis 8 obovatis magnis (lin. 8–9 longis); pappo e paleis 1–2 subulatis aristiformibus 4–3 brevibus oblongis truncatis. — Abundant in hilly districts southeast of San Luis Potosi, forming dense bunches. A showy species. No. 504.

PEREZIA PARRYI. *P. nanæ* proxima, multicaulis; caulibus ramisve subsimplicibus spithamæis usque ad apicem monocephalum foliosis; foliis parvulis (lin. 6–9 longis) obovatis oblongisve basi angusta sessilibus margine spinuloso-dentatis, summis capitulum involucrentibus; involucre 15-floro, bracteis cuspidato-acuminatis, extimis ovatis; acheniis (etiam ovariis) glaberrimis. — Gravelly hills near San Luis, also at Saltillo, in clumps. No. 545.

PEREZIA COULTERI. Herbacea, fere glabra; caule (ramo?) gracili simplici (2–3 ?-pedali) apice in cymam nudam laxè polycephalam deliquescente; foliis tenuiter papyraceis angusto-oblongis utrinque ob-

tusis sessilibus margine denticulatis vel integriusculis, rete laxa vix prominula; capitulis pedicellatis parvulis (vix semipollicaribus); involucri 6-7-floro pauciseriali e bracteis oblongo-linearibus obtusis lin. 2-3 longis cum paucis exterioribus brevioribus ovalibus; corollis ut videtur roseis; acheniis minute glanduloso-puberulis. — Gravelly slopes, near San Luis, flowering in spring and again in autumn. No. 547, in part. This is no. 234 of Coulter's Mexican collection, from Zimapan; and the species seemingly has not before been taken up. In the distribution it was accompanied by the following.

*PEREZIA OXYLEPIS*. Herbacea, puberula, subglanduloso-scabrida, ramosa; ramis patentibus foliosis laxè paniculato-polycephalis; foliis (superioribus) tenuiter papyraceis oblongis acutis creberrime spinuloso-denticulatis basi auriculis laciniato-dentatis subclausis amplexicaulibus, venis primariis prominulis parum reticulatis; capitulis pedicellatis (lin. 9 longo); involucri 14-16-floro pauciseriali; bracteis omnibus lanceolatis tenuiter acuminatis dorso glanduloso-puberis (intimis semipollicem longis); acheniis glanduloso-pubescentibus. — No 547 in part. In the distribution of Liebmann's plants from Copenhagen, his 351 is said to consist of "*Acourtia carpholepis* and *A. oxylepis*, Sch. Bip." We possess only the former. That has such resemblance to the plant here characterized that I venture to take up the latter name, which in any case is appropriate to the present plant.

## 2. Some New North American Genera, Species, &c.

### SUKSDORFIA, Nov. Gen. *Saxifragearum*.

Calycis tubus campanulatus, ovario adnatus, ultra eum vix productus; lobis 5 angustis (sæpe attenuati) erecti, æstivatione leviter imbricati. Petala 5, sinubus calycis inserta, longe unguiculata, marcescenti-persistentia, lamina oblongo-lanceolata vel spathulata, nunc integra nunc 1 vel 2 trilobata, æstivatione imbricata. Stamina 5, petalis alterna: antheræ subsessiles, breves. Ovarium inferum, biloculare, apice breviter birostre: stigmata truncata. Capsula ovalis, calycis lobis conniventibus coronata, inter rostra dehiscens; placentæ axiles polyspermæ. Semina subquadrata, angulis scabridis exceptis lævia. Embryo in axi albuminis parvus. — Herba tenera, viscidulo-pubens, *Saxifragis Nephrophyllis* sat similis; radice bulbilifero-granulifera; foliis radicalibus reniformi-rotundatis lobatis petiolo basi dilatata setifero, caulinis inferioribus petiolo basi quasi foliaceo-stipulatis, superioribus quasi panduratis, basi stipuliformi amplexicauli crenato-incisa

lamina propria obovata sæpius majore; anthela nuda paniculæformi pauciflora, pedicellis ebracteatis; corolla læte violacea. Flos raro 7-merus gynæcio trimero.

**SUKSDORFIA VIOLACEA.** Wet rocks on the Columbia River, in Washington Territory, near the junction of the White Salmon River, W. Suksdorf, April, 1878; also on the Oregon side of the river, Joseph Howell, June, 1879. An interesting new member of the group to which *Sullivantia* and *Boykinia* belong, dedicated to the first discoverer, whose collections and notes prove him to be an intelligent botanist and an acute observer.

#### CARPENTERIA, Torr., char. emend.

Calycis tubus crateriformis; lobis 5 (raro 6-7) valvatis persistentibus. Petala totidem, æstivatione imbricata, rotundato-obovata, demum oblonga, sero decidua. Stamina numerosissima: filamenta filiformia: antheræ innatæ, breves, basi apiceque emarginatæ. Ovarium subdepressum, stylo brevi crasso superatum, medio calycis tubo adnatum, sæpius 5-loculare (loculis petalis antepositis): stigmata 5, oblonga, coadunata, singulis bilobis, lobis parallelis connatis. Capsula conica, præter basim latam depressam supera, stylo brevi (demum a basi sursum fisso) apiculata. Cæt. fere *Philadelphus*.

**CARPENTERIA CALIFORNICA**, Torr. in Pl. Fremont. 12, t. 7, was described from fruiting specimens, with some vestiges of flower, collected in the southern part of the Sierra Nevada, California, by Fremont, in the year 1849, or thereabout. No other specimens had come to hand until now received from Dr. Kellogg, with good flowers, flower-buds, and fruit. These were collected by Dr. Eisen on King's River, in Fresno Co., in 1877. From them I here complete the character. The interesting points determined are:—1. That the petals are quincuncially imbricated in the bud. Dr. Torrey had no flower-bud; the character "æstivatione convoluta" may have been supplied by the analogy of *Philadelphus*. 2. The ovary, which in the unopened flower is, as it were, depressed-biconical, and rather broader than high, has the flattish calyx-tube adnate to its middle and to the level of the attachment of the projecting placentæ to the axis. But the upper part enlarges and lengthens, so that in fruit the capsule is almost wholly free. 3. I do not find the stigmas "distinct," nor even separable in the fruit. They are all coalescent into a compound stigma which is 10-sulcate (of two parallel lobes to each particular stigma), and this remains undivided, holding the tips of the component styles together after they have been riven asunder below by the

dehiscence of the capsule. The genus should probably be upheld, but the distinctions between it and *Philadelphus* are rather slight. Two of them are now brought out, namely, the imbricative æstivation of the corolla (but this sometimes occurs in *Philadelphus*), and the structure of the stigma, which so far as I know is not imitated in *Philadelphus*. The more superior gynœcium is striking, at least in fruit; but that is a matter of degree. The habit and foliage in this plant and in *Philadelphus serpyllifolius* are not unlike. Occasionally the petals and some of the filaments persist until the fruit is grown.

HOWELLIA, Nov. Gen. *Lobeliacearum*.

Flores bifformes, pedunculati, emersi amplius corolliferi, submersi corolla depauperata. Calycis tubus lineari-clavatus, usque ad summum apicem ovarii adnatus; limbo 5-secto, segmentis subæqualibus. Corolla calycem haud superans, tubo brevissimo hinc fissio, lobis oblongis subæqualibus, tria in labium trifidum altius coalitis. Staminum tubus fere liber, cum stylo leviter incurvus: antheræ ovales, duo minores setulis 3 penicillatæ, tres majores nudæ: stigma bilobum. Ovarium prorsus uniloculare: placentæ 2 filiformes parietales, pauci-(3-5-) ovulatæ: ovula superiora adscendentia, inferiora pendula. Capsula clavato-oblonga vel fusiformis, apice contracta, matura membranacea, uno latere irregulariter rumpens. Semina pauca, lineari-oblonga, ratione capsulæ magna (lin. 2 longa). lævia, ad chalazam calloso-subapiculata. — Herba aquatica; nunc tota submersa, ramis verticillatim ortis elongatis foliosissimis, foliis lineari-setaceis elongatis plerisque alternis, floribus axillaribus fere cryptopetalis, capsula lineari-fusiformi calycis lobis lineari-setaceis elongatis superata; nunc apice emersa, foliis subremotis parvis lineari-oblongis sæpe 1-2-dentatis, calycis lobis linearibus sesquilineam longis corollam albam subæquantibus, capsula breviora in pedunculo parum longiore.

HOWELLIA AQUATILIS. — In stagnant water, on Sauvies Island in Willamette Slough, Oregon; discovered by Thomas T. and Joseph Howell, who collected in May, 1879, the submersed form, abundantly flowering and fruiting, but the inconspicuous corolla hardly expanding; and in August, at another station, specimens with emerged tips to the stems, bearing flowers with well-developed corolla, but much shorter calyx-lobes. This corolla is a line and a half or two lines in length, the limb that of a *Lobelia*, but with the tube very short and the slit between the two (seemingly) upper petals extending to the base, yet apparently not quite separating them. At the other margin these two petals are manifestly connate with the adjacent ones of the

three-cleft spreading lip. The only mature capsule seen belonging to an emersed flower is hardly over three lines long and clavate-oblong. Immature submersed capsules are of double this length and fusiform, their setaceous calyx-lobes commonly three lines long. The ovary is strictly one-celled from the first. The submersed plant has somewhat the aspect of *Naias flexilis* or a narrow-leaved *Anacharis*; the stems a foot long; the leaves an inch or two long, and a third or a fourth of a line wide. These are alternate, tending occasionally to opposite and verticillate, generally quite entire, but sometimes with one or two lateral teeth. The emersed leaves seen are only two lines long, and are not unlike those of *Downingia pulchella*. Possibly this new plant might be brought under that genus, but not with propriety. Besides the sessile long-linear ovary, the unisetose anthers, and the great inequality of the two lips of the corolla, the tube in that genus is more deeply cleft laterally than between the two small petals. Our plant must accordingly be received as a new generic type, allied to *Lysipomia*, HBK. (*Lysipoma*, A.DC.), *Downingia*, and somewhat to *Laurentia*, but not referable to any of them. It is dedicated to the discoverers, who are assiduous collectors and acute observers, and who have already much increased our knowledge of the botany of Oregon.

NEWBERRYA, Torr., char. auct.

Sepala bracteoliformia 2 vel 4, linearia. Corolla tubo intus cum filamentis stylisque villosa. Discus hypogynus e dentibus deflexis inter stamina 8-10. Cæt. in char. spec.

NEWBERRYA CONGESTA, Torr. Floribus crebre cymoso- (corymbiformi-) congestis; corollæ lobis ovatis tubo cylindraceo suburceolato triplo brevioribus; filamentis stylo gracili æquilongis; antheris angusto-oblongis, loculis rima connectivo proxima dehiscentibus; squamis caulinis ovatis obtusis parum erosis. — Known from Dr. Newberry's advanced and imperfect specimens from Des Chutes valley in the Cascade Mountains, S. Oregon, and now (1878) collected by V. Rattan, in Fir (Douglas Spruce) forests, on the north fork of Mad River, in Humboldt Co., California, in fine flowering state, with corymbiform-glomerate inflorescence on a very short stem, of only an inch or two in height. The lower scales are apparently rather broader than in Newberry's plant. The specimen collected by the late George Gibbs apparently belongs to the following species.

NEWBERRYA SPICATA. Floribus spicato-congestis; corolla magis campanulata, lobis oblongis tubo dimidio brevioribus; filamentis stylis ovario vix longiorem haud æquantibus; antheris brevi-oblongis, loculis



rima a connectivo parum remota; squamis caulinis angusto-oblongis acutiusculis magis fimbriato-erosis. — Humboldt Co., California, V. Rattan. Ten or twelve miles east of the station of the preceding species, and at least a thousand feet higher, associated with *Boschniakia strobilacea* and *Allotropa virgata*. Washington Territory, George Gibbs. In the earlier state the plant bears a singular resemblance to *Pleuricospora fimbriolata*.\*

RANUNCULUS MACAULEYI. E grege *R. nivalis*; foliis diversissimis, nempe omnibus integris lingulatis, apice truncato tridentato, radicalibus (pristinis oblongis) in petiolum attenuatis, caulinis sessilibus; sepalis extus nigricanti-villosissimis; petalis aureis; carpellis in stylum brevem subulatum attenuatis. — Rocky Mountains in San Juan Co., Colorado, Lieut. C. H. McCauley, U. S. A., Mr. F. N. Pease. Lieut. McCauley collected two specimens of this most distinct species in the summer of 1877, but with only the blossom and upper leaves. The flowers so exactly resembled those of *R. nivalis* in the typical arctic-alpine form and with very dark villous calyx, that I entered it under that name in the catalogue of the plants of his collection, just now published by the Engineer Department in the report of an official exploration of the region. But Mr. Allen of Yale College now sends us two complete specimens, showing the remarkable foliage. These were collected "about Crystal Lake, San Juan Co., at 11,700 feet of elevation, July 8, 1878," by his correspondent *F. N. Pease*. All that is now wanted is the fruit, which we trust Mr. Pease will supply. From the blossom it may be conjectured that the head of mature carpels may be oblong; and these are more gradually attenuated into a shorter style than in *R. nivalis*. The petals in the specimens are light yellow. Lieut. McCauley displayed such zeal and activity in making a botanical collection under many difficulties, and is likely in future explorations to turn his experience to such good account for our science, that it is with much pleasure that I avail myself of the opportunity now afforded to name this species in honor of its first discoverer.

CARDAMINE CLEMATITIS, Shuttleworth in coll. distrib. Rugel. Spec. distinctissima, glaberrima, semi-subpedalis e rhizomate tenero; foliis radicalibus primariis reniformibus subintegris, cæteris trisectis (segmentis rotundatis nunc angulatis, terminali majori reniformi-cordato seu angulato-trilobo) vel supremis oblongatis trilobis, petiolo

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\* *Boschniakia strobilacea*, Gray, was abundantly found by Mr. Rattan in the same district. The seeds have a deeply foveose coat.

basi dilatata insigniter sagittato-appendiculato, auriculis subulatis; racemo brevi laxo; petalis albis (lin. 3 longis) calyce plus duplo longioribus; siliqua angusto-lineari compressa in stylum sat longum attenuata; stigmatibus parvo. — Wet ground along streamlets in the higher Iron or Smoky Mountains of North Carolina and Tennessee, collected in 1844 by Rugel, and about the same time by Buckley; common in the higher wooded parts of Roan Mountain, where it was collected in June, 1879, by Messrs. Canby, Redfield, Sargent, and myself. A specimen from Buckley was by me confounded with *C. rotundifolia*, and is the only authority we know of for attributing to that species occasionally trisected leaves, as is done in the Manual of the Botany of the Northern States. An imperfect original specimen from Shuttleworth was mixed up with a Florida species, intermediate between *Cardamine* and *Nasturtium*, first received from Leavenworth without fruit, and referred in the Supplement to the first volume of Torrey & Gray's Flora to *N. officinale*; it was afterwards received from Buckley, then from Shuttleworth (coll. Rugel), first as *Cardamine curvisiliqua*, Shuttl., and again as *Nasturtium stylosum*, Shuttl. Lately it has been sent by Dr. Garber.

**ASTRAGALUS REVENTUS.** PHACA, *Scytocarp*i, pedalis e radice perenni, minute pubescens; stipulis parvulis liberis scariosis; foliis 10–18-jugis oblongis seu lineari-oblongis emarginatis supra glabellis (semipollicaribus); pedunculis elongatis; spica brevi-oblonga densiflora; floribus patentibus nunc deflexis; calyce oblongo-campanulato nigricanti-pubescente, dentibus subulatis tubo parum brevioribus; corolla sordide alba (carina apice sæpius violacea)  $\frac{3}{4}$ – $\frac{1}{2}$ -pollicari; leguminibus in pedicello brevi arrectis haud stipitatis cartilagineis glabris ovato-oblongis rectis turgidis (lin. 8–10 longis) apiculato-cuspidatis prorsus unilocularibus, suturis angustis haud intrusis extus parum prominulis. — “Interior of Oregon,” coll. Douglas, in fruit. Mentioned in Torr. & Gray, Fl. i. 694, and in Proc. Am. Acad. vi. p. 234. Now collected in Grand Round Valley and Blue Mountains in the eastern part of Oregon, in April, 1878, in flower and with forming fruit, by William C. Cusick; and, about the same time, in Klikitat Valley, Washington Territory, by Joseph Howell. No other of the thick-walled *Phacæ* much resembles this now completely identified species.

**ASTRAGALUS HOWELLI.** *Galegiformes* post *A. Drummondii*, cinereo-pubescent; caule gracili bipedali; foliis subsparsis; foliolis multi-jugis oblongis (haud semipollicaribus); pedunculis elongatis strictis; racemo multifloro; pedicellis brevibus bractea tenui subulata sequi-

longis; floribus mox pendulo-reflexis; calyce basi vix gibboso, dentibus setaceo-subulatis tubo parum brevioribus; corolla ochroleuca; leguminibus pendulis canescentibus pollicaribus oblongo-lanceolatis utrinque acutatis bilocellatis stipite vix duplo longioribus, sectione transversa cuneato-obcordata. — Wasco County, S. E. Oregon, Joseph Howell.

**ELEPHANTOPUS NUDATUS.** Hirsutulo-pubescens, viridis; foliis plerisque radicalibus humifusis oblongis spathulato-obovatis oblanceolatisque, venis parum prominulis; caule scapiformi subaphyllo; glomerulis parvulis; setis pappi basi brevissime abrupte deltoideo-dilatatis. — *E. scaber*, Torr. & Gray, Fl. ii. 61, non Linn. *Echinophora* affinis Mariana, Scabiosæ pratensis folio integro, capitulo splendente lævi, summo caule coronata, Pluk. Mant. 66, t. 388, fig. 6? — This we have from "Oxford, Delaware, and thence common southward," Canby; near Snow Hill, Maryland, Bebb, collected by both botanists in September, 1863. From the habitat and from the rude figure we may refer to this the plant of Plukenet above cited, which Gronovius in the second edition of the Flora Virginica referred to Clayton's *E. foliis obverse lanceolato-oblongis rigidis, &c.*, and confused with *E. scaber*. We have a doubtful (because immature) specimen from South Carolina; and the specimens of Hale from Louisiana, referred to *E. scaber* in Torr. & Gray, Flora, above cited, are clearly of this species. In habit this resembles *E. tomentosus*, but it has none of the canescently silky minute pubescence which distinguishes the foliage of that species; the glomerules are smaller, and the scale-shaped base of the setæ of the pappus is remarkably short, small, and broad. The only species resembling it in this respect is the Tropical American *E. mollis*, HBK. The latter has the soft pubescence of *E. tomentosus* and the leafy stem of *E. Carolinianus*. Thus we recognize three fairly distinct species in the United States, all peculiar to the country. *E. mollis* is the tropical American species, and *E. scaber* the species of the Old World tropics, but naturalized in the West Indies, &c. In the twentieth volume of the Linnæa, Schultz (Bipontinus) united all these allied American species, but was disposed to keep the Old World *E. scaber* separate. Grisebach, in the Flora of the British West Indies, distinguished *E. scaber*, *E. mollis*, and *E. Carolinianus* as so many species. But Baker, in the Flora Brasiliensis, takes *E. mollis* to be identical with *E. tomentosus* and no more than a mere variety of *E. scaber*. In our view all five species may be critically distinguished.

LEPTOCLINIUM. (*Liatris* § *Leptoclinium*, Nutt.)

Capitulum pauciflorum. Involucrum fere pentasticho-imbricatum (§), bracteis exterioribus gradatim brevioribus subherbaceis. Receptaculum parvum, nudum. Corolla fauce infundibuliformi-ampliata e tubo gracili; lobi angusto-lanceolati necnon achenia *Liatridis*. Pappus e setis tenuioribus copiosis biseriatis barbellato-serrulatis inæqualibus, exterioribus brevioribus. — Frutex 4–6-pedalis (Floridanus), fastigiato-ramosus; foliis alternis (infirmis oppositis ex Nutt.) obovatis coriaceis fere eveniis pallidis concoloribus (verticalibus) cauli articulatis; capitulis corymboso-cymosis.

LEPTOCLINIUM FRUTICOSUM. — *Liatris fruticosa*, Nutt. — Coast of S. Florida, *Ware, Garber*. If the lower leaves are indeed opposite, the genus is the more confirmed.

LIATRIS GARBERI. Pilis multi-articulatis hirsuta; foliis mox glabris rigidis linearibus, summis lineari-subulatis; capitulis crebre spicatis 6–7-floris (majoribus semipollicaribus); involucri campanulato 10-phylo, bracteis ovatis oblongisque mucrone cuspidato-apiculatis dorso viridulis creberrime glandulosis hirsutis demum glabris; pappo (lin. 3 longo) barbellulato. — Near Tampa, Florida, Dr. A. P. Garber, September, 1877.

BACCHARIS PLUMMERÆ. Herbacea, tomentuloso-pubescent; caulibus 2–3-pedalibus simpliciusculis apice cymoso-polycephalis; foliis spathulato-linearibus sessilibus (vix pollicaribus) rigidis argute serratis subtrinerviis supra glabris; capitulis fere hemisphæricis (lin. 3–4 altis); bracteis involucri herbaceo-membranaceis lanceolatis obtusiusculis margine leviter scariosis dorso pubescentibus 3–4-seriatim imbricatis; corollæ fl. fœm. limbo irregulariter laciniato-partito stylum subæquante tubo 2–3-plo brevior, laciniis lineari-subulatis nunc incis; pappo fœm. rigidulo scabro corollam stylumque paullo excedente. — Along a stream in Glen Loch ravine, in the mountains near Sta. Barbara, California, where also grows *Palmarella debilis*; discovered by Miss S. A. Plummer, an ardent botanist, whose name it is a pleasure to commemorate.

RHODODENDRON (AZALEA) VASEYI. Dumosus; ramis glabris; perulis paucis; foliis membranaceis parce pubescenti-pilosis mox glabris ovato-oblongis acuminatis basi acutis; pedicellis gracilibus glandulosis post anthesin recurvatis; calyce brevissimo truncato; corolla rosea rotato-campanulata subæqualiter fere 5-partita extus intusque glaberrima, lobis obovatis; staminibus 5 inæqualibus, longioribus styloque corollam paullo excedentibus; ovario subglanduloso;

capsula glabrata oblonga. — Balsam Mountain, seven miles southwest of Webster, Jackson County, North Carolina, coll. George R. Vasey, June 3, 1878, in blossom. The American Azaleas previously known consist of one aberrant species, *R. Rhodora*, and of a well-marked group (to which *R. Ponticum* also belongs) characterized by a long-tubed funnel-form corolla and long exserted stamens and style. But the East Asiatic species of the same true *Azalea* subgenus have campanulate or rotate-campanulate corollas, and some of them very deciduous *perulae* to the separate flower-buds. This most interesting new species is one of that group, and it thus adds another to the now very numerous cases of remarkable relationship between the Chino-Japanese and the Alleghanian floras. It most resembles *R. Albrechti*, a subalpine species of Japan; but is pentandrous, smoother, not at all setose, smaller-flowered, the corolla (about an inch long) glabrous within as well as without; and the leaves are not obovate or so cuneate at base. As this interesting accession to our flora is one of the fruits of a botanical tour recently made by Mr. George R. Vasey, son of Dr. Vasey, the botanist of the Agricultural Department, who recognized its novelty and placed a specimen in my hands, I seize the opportunity of commemorating the name of Vasey in connection with the noble genus *Rhododendron*.

PHACELIA (MICROGENETES) COOPERÆ. *P. bicolori* et *P. gymnocladæ* proxima, pube densa viscida subcinerea; foliis oblongis obtusis crenato-subpinnatifidis petiolo subæquilongis; floribus plerisque sessilibus densius spicatis; corolla tubuloso-infundibuliformi calycis lobis 2-3-plo longiore, limbo cæruleo seu violaceo, tubo fauceque angustis flavis, appendicibus angustis a filamento liberis; ovulis 7-8. — California, in the Santa Inez Mountains, Santa Barbara Co., Mrs. Ellwood Cooper. This is the only species of the *Microgenetes* section found west of the Sierra Nevada. The seeds in the specimen, although not mature, indistinctly show the transverse corrugations. The corolla is nearly half an inch long, and is even more tubular than that of *P. bicolor*; the filaments are attached almost to its base and barely connected with the very base of the narrow plicæ.

BREWERIA GRANDIFLORA. Sericeo-puberula; caulibus e radice tuberosa procumbentibus; foliis brevissime petiolatis late ovalibus subæqualiter penniveniis, majoribus (sesquipollicaribus) apice nunc utrinque retusis; pedunculis unifloris folio brevioribus; sepalis lanceolatis acutiusculis, 2 exterioribus paullo brevioribus; corolla cærulea (tripollicari!) infundibuliformi tubo extus villosulo; stylis capillaribus a basi fere discretis; stigmatibus majusculis globosis;

seminibus glabris. — Manatee and Sarasota, S. Florida, Dr. A. P. Garber, June, 1878, in flower. This striking species has the habit of the little known *B. ovalifolia* of the Mexican border, and of *B. Menziesii* of the Sandwich Islands. The remarkably large flowers are said by the discoverer to be bright blue and very showy.

**COLLINSIA RATTANI.** Caule stricto 8–12-pollicari puberulo superne pedicellis calyceque pl. m. glandulosis; foliis fere glabris, caulinis angusto-linearibus (lin. 6–14 longis) plerumque integerrimis, imis spathulatis parvis; pedicellis 2–4-natis (lin. 3 longis) flore parvo æquilongis; calycis lobis lato-lanceolatis obtusiusculis; corolla (roseo-violacea) parum declinata, labiis (lin. 1–2 longis) fauci cum tubo adæquantibus, posticos basi bicalloso; staminodio subulato; ovarii loculis 1–2-ovulatis; capsula calyci æquilonga; seminibus meniscoideis marginatis. — Open hillsides south of Trinity River, &c., N. W. California, V. Rattan (1878–9), Greene (1876); also in Simcoe Mountains, Oregon, Joseph Howell, 1879. Flowers no larger than those of *C. parviflora*; stem strict and mostly simple in the manner of *C. Parryi*.

**COLLINSIA LINEARIS.** Pedalis; foliis caulinis linearibus obtusis integerrimis sessilibus elongatis (poll.  $1\frac{1}{2}$ –3 longis lin. 1–2 latis) cum caule ramisque glabris, imis lanceolato-spathulatis subdentatis; pedicellis filiformibus 2–4-natis flore sæpius æquilongis cum calyce (lobis triangulari-lanceolatis acutis) glanduloso-puberulis; corolla (dilute cærulea semipollicari) maxime declinata et gibboso-saccata, labiis fauce tuboque longioribus, postico basi callo prominulo nunc bilobo instructo; filamentis glabris; staminodio filiformi-subulato; ovarii loculis 3-ovulatis; seminibus meniscoideis. — Along the Klamath and Trinity Rivers, on argillaceous-rocky hills, N. W. California, 1878 and 1879, V. Rattan. A taller, more branching, and larger-flowered species than *C. Torreyi*, to be ranked in the section with *C. grandiflora* and *C. sparsiflora*, yet with the inflorescence, &c. minutely and slightly glandular. A form with violet corolla was gathered near Waldo, Oregon, just over the State line.

**PENTSTEMON RATTANI.** *Genuini*; caule 1–3-pedali, inferne glabro, superne cum thyrso calycibusque viscoso-pubescente; foliis membranaceis argute sæpius creberrime denticulatis oblongo-lanceolatis, inferioribus basi attenuatis, superioribus sæpe ovato-lanceolatis basi subcordata semiamplexicaulibus (majoribus poll. 4–8 longis); thyrso laxo, cymis inferioribus pedunculatis 5–8-floris; pedicellis brevissimis; sepalis oblongo-lanceolatis subacuminatis laxis; corolla pollicari pallido-purpurea, fauce obliqua e tubo proprio calyce paullo breviora

campanulato-ampliata, labio inferiore intus villosa-barbato; antheris filamentisque glabris; filamento sterili subexserto hinc longe parceque barbato. — N. W. California, on Humboldt Ridge, Humboldt Co., 1878 and 1879, in a spruce forest, V. Rattan. The upper part of our plant is, in general, not badly represented by the figure of *P. campanulatus* in Bot. Mag. t. 3884, which seems to be *P. perfoliatus*, Brongn., a Mexican species. It is very unlike any other Californian species, and is dedicated to the discoverer, who began his contributions of materials for the flora of that State several years ago, and has now for two summers devoted his vacation to the botanical exploration of its northwestern counties with gratifying success. Mature fruit has not yet been collected; but partially-formed capsules show forming seeds with an apparently loose cellular coat, investing a small nucleus. Its seeds may, therefore, be not unlike those of an anomalous species of the forests farther north, *Chelone nemorosa* of Douglas, which Trautvetter transferred to *Pentstemon*, and which in Syn. Fl. N. Am. ranks as a subgenus, *Nothochelone*. Its seeds are really not those of *Chelone*, and the two genera might be better defined by transferring this connecting section to *Pentstemon*. But mature seeds of the present species should first be examined.

Var. MINOR is apparently a depauperate state or form of the present species with flowers one half smaller. Collected on Indian Creek, Del Norte County, California.

ORTHOCARPUS BIDWELLÆ. *Triphysaria*, facie *O. erianthi*, Benth.; spica laxiore; corolla graciliore, fauce cum galea atropurpurea, labio trisaccato late aureo; testa seminum laxa arilliformi cellulosa. — California; near Chico, Mrs. John Bidwell; near Auburn, Placer Co., Mrs. Pulsifer-Ames. — Within a few weeks after the publication of the first part of the Synoptical Flora of North America, which contains this already large genus, we received, almost simultaneously from these two sources, specimens of this well-marked new species. The name of Mrs. Ames is well known in Californian Botany, to which she has made many interesting contributions. Let this neat species commemorate its other discoverer, Mrs. Bidwell, from whom we have received excellent collections, made by General Bidwell and herself upon their own ranche at Chico, and upon the mountains toward the sources of Chico Creek. In foliage this species is hardly distinguishable from *O. erianthus*, although somewhat less pubescent; the filiform tube of the corolla is even more slender, over half an inch long; and the trisaccate lip is rather smaller, of a bright golden yellow color, while the throat as well as the galea is dark purple.

All the anthers are one-celled ; but the seeds, instead of the close coat of all the other species of that group, have the nucleus surrounded by the loose and cellular arilliform coat of the other section. Between these two subsections this species has to be intercalated.



## IV.

ON THE ESTIMATION OF PHOSPHORIC ACID AS  
MAGNESIC PYROPHOSPHATE.

By F. A. GOOCH.

Presented October 8th, 1879.

THE investigation of which this paper is an account was undertaken at the request of Dr. Wolcott Gibbs, for the purpose of finding, for use in his work upon the complex inorganic acids, the best mode of proceeding in determining the phosphoric oxide of phosphotungstates and phosphomolybdates by precipitation as ammonio-magnesian phosphate and estimation as magnesian pyrophosphate. During the course of the work it has been found necessary to review much of what has been previously published concerning this method of determining phosphoric acid.

In a paper upon this subject, Kubel \* criticised Fresenius's correction † (subsequently withdrawn ‡) for the solubility of ammonio-magnesian phosphate in water containing free ammonia and magnesia mixture, and asserted that such correction is not only unnecessary, but that the results of the analysis are of themselves much higher than theory indicates unless the precipitate is, after washing, dissolved and reprecipitated. Kubel's method was to add hydrochloric acid and then ammonia, or ammoniac chloride, or ammonia, to a measured amount of a solution of sodic phosphate, to precipitate with magnesian sulphate mixture, and after twelve hours to filter off and wash with dilute ammonia containing one part of strong ammonia to three of water. A number of analyses made in this way gave amounts of phosphoric oxide varying from 101.5 to 104.3 per cent. of the real quantity present,—the actual weight being in each case 0.1986 gr. Another set of analyses in which the precipitate was, after washing, dissolved in hydrochloric acid and again thrown down with ammonia,

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\* Zeitschrift für Anal. Chem., VIII., 125.

† Anleitung zur Quant. Anal., 5 Aufl., 388.

‡ Ibid., 6 Aufl. 134.

but which were otherwise treated in the same manner as the first, gave figures for phosphoric oxide varying from 99.8 per cent. to 100.5 per cent. of the real amount. When the precipitate was twice dissolved and twice reprecipitated, the amount of phosphoric oxide indicated was 99.8 per cent., and when three times dissolved and reprecipitated, 99.2 per cent. of the real amount. While noting that the precipitate is not absolutely insoluble in ammonia, more especially if it contain ammoniac chloride, Kubel concludes, supposing that a basic sulphate or hydrate of magnesium is thrown down with the first precipitate, that this precipitate must be dissolved after washing and again thrown down with ammonia.

Kissel,\* by using large amounts of ammoniac chloride, washing copiously in order to make the solubility of the precipitate compensate for the inclusion of foreign matter, and taking care to use no great excess of the magnesian sulphate mixture, obtains in one set of experiments from 99.4 to 99.6 per cent., in another from 99.8 to 100 per cent., of the correct amount of phosphoric oxide. Of three filtrates from the precipitated ammonio-magnesian phosphate two gave weak reactions for phosphoric acid with acid ammoniac molybdate, and one no reaction. The wash-water tested by the same method gave in every case a plain reaction. Heintz † supports Kubel so far as to say that in presence of any considerable excess of magnesian sulphate mixture the precipitate must be dissolved after incomplete washing. Brunner ‡ points out that the solution must not be precipitated hot by magnesian sulphate mixture on account of the danger of throwing down magnesian hydrate. Schumann § supports Kissel in the view that the solution of the first precipitate is unnecessary, but adds a caution against the addition of ammonia after the magnesian sulphate mixture.

Finally, Abesser, Jani, and Märcker || substantiate Kubel's results, and having proved the presence of a sulphate in the precipitate obtain somewhat better figures by igniting over the blast. Adopting the method of precipitating by magnesian chloride mixture previously suggested by Brassier ¶ and Bunsen,\*\* and recommended in the works

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\* Zeitschrift für Anal. Chem., VIII. 169.

† Ibid., IX. 16.

‡ Ibid., XI. 30.

§ Ibid., XI. 382.

|| Ibid., XII., 239.

¶ Ann. de Chim. et de Phys. [4] VII. 385.

\*\* Zeitschrift für Anal. Chem. X. 405.

of Rose\* and Fresenius,† their analyses show from 99.96 per cent. to 100.48 per cent. of the true amount of phosphoric oxide. The weight of phosphoric oxide used in each of their experiments was not far from 0.1250 gr. The precipitate was washed until the reaction for chlorine with argentic nitrate failed to appear in the filtrate acidified with nitric acid. The method of precipitating with magnesian chloride and igniting over the Bunsen lamp gave in their hands from 99.96 to 100.48 per cent.; the method of precipitating with magnesian sulphate and igniting over the blast, from 100.4 to 100.7 per cent.; and the method of precipitating with magnesian sulphate and igniting over the Bunsen lamp from 101.4 to 103.1 per cent. of the actual amount of phosphoric oxide.

All agree that the precipitated ammonio-magnesian phosphate is soluble to a very considerable extent in dilute ammonia, and to a greater extent in ammonia containing ammoniac chloride; that the presence of a magnesian salt tends to prevent the solution of the precipitate; and that when magnesian sulphate is used in excess as a precipitant the precipitate includes, mechanically or otherwise, an appreciable amount of magnesian sulphate, or magnesian hydrate, or both. Kiesel and Schumann aim to arrive at correct results by precipitating with as little excess of magnesian sulphate mixture as possible, and compensating for foreign inclusions by dissolving a part of the precipitate. Kubel and Heintz strive to reach the same end by removing the excess of the precipitant, together with the included impurity by filtering off, dissolving, and again throwing down the precipitate.

With this preface I proceed to the description of my own experiments upon this subject.

I have worked with measured portions of solutions of hydro-disodic phosphate, or of microcosmic salt, the standards of which were, in all cases but one, determined by evaporating a known volume to dryness, igniting the residue and weighing the remaining sodic pyrophosphate or metaphosphate as the case might be. In the one exceptional case a known weight of microcosmic salt, freshly crystallized and dried, the volatile constituents of which had been determined by igniting separate portions, was dissolved in a known volume of water. The experiments which fixed the standards of these solutions are given below.

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\* Rose's *Analytische Chemie*, VI. Aufl., 512, bearbeitet von Finkener.

† *Anleit. zur Quant. Anal.* 6 Aufl. 408.

## I.

Two portions of 20 cm.<sup>3</sup> each of a solution of hydro-disodic phosphate were evaporated to dryness, and the residue was ignited and weighed as sodic pyrophosphate.

(1) gave of  $\text{Na}_4\text{P}_2\text{O}_7$  0.1217 gr.

(2) " " 0.1214 gr.

The solution contained, therefore, 0.1298 gr. of  $\text{P}_2\text{O}_5$  to every 40 cm.<sup>3</sup>.

## II.

A quantity of microcosmic salt was recrystallized, dried between papers by pressure, and the amount of loss on ignition determined in two portions.

(1) 1.1419 gr. gave of  $\text{NaPO}_3$  0.5836 gr. = 51.11 %

(2) 0.9846 gr. " " 0.5027 gr. = 51.06 %

Of this salt 3.7583 gr. were dissolved in water and the solution diluted to one litre. The solution contained, therefore, 0.0512 gr. of  $\text{P}_2\text{O}_5$  to every 40 cm.<sup>3</sup>.

## III.

The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 40 cm.<sup>3</sup> 0.3490 gr.

(2) " " " " 0.3490 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.1863 gr.  $\text{P}_2\text{O}_5$ .

## IV.

The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 40 cm.<sup>3</sup> 0.3530 gr.

(2) " " " " 0.3533 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.1885 gr.  $\text{P}_2\text{O}_5$ .

## V.

The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 40 cm.<sup>3</sup> 0.3512 gr.

(2) " " " " 0.3514 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.1875 gr.  $\text{P}_2\text{O}_5$ .

## VI.

The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 40 cm.<sup>3</sup> 0.4112 gr.

(2) " " " " 0.4113 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.2195 gr.  $\text{P}_2\text{O}_5$ .

## VII.

The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 40 cm.<sup>3</sup> 0.3429 gr.

(2) " " " " 0.3429 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.1831 gr.  $\text{P}_2\text{O}_5$ .

## VIII.

The solution contained microcosmic salt.

(1) gave  $\text{NaPO}_3$  from 40 cm.<sup>3</sup> 0.3077 gr.

(2) " " " " 0.3078 gr.

Every 40 cm.<sup>3</sup>, therefore, contained 0.2142  $\text{P}_2\text{O}_5$ .

## IX.

The solution contained microcosmic salt.

(1) gave  $\text{NaPO}_3$  from 40 cm.<sup>3</sup> 0.2897 gr.

(2) " " " " 0.2900 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.2017 gr.  $\text{P}_2\text{O}_5$ .

## X.

The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 20 cm.<sup>3</sup> 0.0247 gr.

(2) " " " " 0.0249 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.0265 gr.  $\text{P}_2\text{O}_5$ .

## XI.

The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 20 cm.<sup>3</sup> 0.0249 gr.

(2) " " " " 0.0250 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.0266 gr.  $\text{P}_2\text{O}_5$ .

## XII.

The solution consisted of 71.5 cm.<sup>3</sup> of Solution IV. diluted to 500 cm.<sup>3</sup> Every 40 cm.<sup>3</sup> contained, therefore, 0.0270 gr.  $P_2O_5$ .

## XIII.

The solution consisted of 71.5 cm.<sup>3</sup> of Solution IV. diluted to 500 cm.<sup>3</sup> Every 40 cm.<sup>3</sup> contained, therefore, 0.0270 gr.  $P_2O_5$ .

## XIV.

The solution consisted of 61.3 cm.<sup>3</sup> of Solution VI. diluted to 500 cm.<sup>3</sup> Every 40 cm.<sup>3</sup> contained, therefore, 0.0269 gr.  $P_2O_5$ .

## XV.

The solution consisted of 61.3 cm.<sup>3</sup> of Solution VI. diluted to 500 cm.<sup>3</sup>. Every 40 cm.<sup>3</sup> contained, therefore, 0.0269 gr.  $P_2O_5$ .

## XVI.

The solution consisted of 125.6 cm.<sup>3</sup> of Solution VIII. diluted to one litre. Every 40 cm.<sup>3</sup> contained, therefore, 0.0269 gr.  $P_2O_5$ .

Each of the following experiments was made with 40 cm.<sup>3</sup> of one or another of these solutions diluted (if necessary), so that the volume after precipitation should for the weaker solutions be about 100 cm.<sup>3</sup>, and for the stronger solutions from 125 cm.<sup>3</sup> to 150 cm.<sup>3</sup>.

Precipitation was effected in cold solutions unless the contrary is stated, and, when not otherwise specified, either by a magnesian sulphate mixture consisting of one part of crystallized magnesian sulphate, two of ammoniac chloride, four of concentrated ammonia, and eight of water; or by a magnesian chloride mixture containing three parts of crystallized magnesian chloride, eight of ammoniac chloride, sixteen of concentrated ammonia, and thirty-two of water. The precipitate of ammonio-magnesian phosphate was, in every case, finally collected on asbestos felt in a perforated platinum crucible according to the process previously described by me,\* washed with 60 cm.<sup>3</sup> to 70 cm.<sup>3</sup> (applied in successive portions) of a solution of one part of concentrated ammonia to three of water, — this amount being found to be more than sufficient for washing, when the asbestos process is used, until the filtrate ceases to show the presence of chlorine when treated with nitric acid and argentic nitrate, — moistened with a

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\* These Proceedings, XIII. 342.

few drops of a solution of ammonic nitrate in ammonia, dried on the vacuum pump, ignited on a platinum crucible-cover, at first gently until fumes of ammonic nitrate no longer appeared, then at a full red heat until the spreading of a glow over the whole residue indicated the formation of the magnesian pyrophosphate.

The results of the experiments are tabulated below. The figures of the first column show the weights of magnesian pyrophosphate found, those of the second the corresponding weights of phosphoric oxide, those of the third the weight of phosphoric oxide required by the determinations of the standard of the solution used, those of the fourth the absolute error in the determination of phosphoric oxide, and those of the fifth the percentage error referred to the actual amount of phosphoric oxide present. The Roman numeral standing against the record of each experiment shows which phosphate solution was used in that experiment.

#### ALKALINE PHOSPHATES.

Experiments (1) to (10) inclusive were made with 40 cm.<sup>3</sup> each of the phosphate solution. Portions (1) and (2) were precipitated with 20 cm.<sup>3</sup> of magnesian sulphate mixture. Portions (3) to (6) were treated with 20 cm.<sup>3</sup> of a magnesian sulphate mixture containing only a small amount of free ammonia, but the same weights of magnesium and ammonium salts as the regular mixture. The first precipitates of (3) and (4) were dissolved in hydrochloric acid and again thrown down by ammonia in presence of the excess of the precipitant, and those of (5) and (6) were dissolved and reprecipitated in this manner twice. Portions (7) to (10) were precipitated with 20 cm.<sup>3</sup> of magnesian sulphate mixture after being acidulated — (7) and (8) with hydrochloric acid, (9) and (10) with 0.5 gr. of citric acid — and made alkaline with ammonia.

	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent error.
I.	(1) 0.2082 gr.	0.1331 gr.	0.1298 gr.	+0.0033 gr.	+2.54
	(2) 0.2113 gr.	0.1352 gr.	0.1298 gr.	+0.0054 gr.	+4.16
	(3) 0.2104 gr.	0.1346 gr.	0.1298 gr.	+0.0048 gr.	+3.70
	(4) 0.2124 gr.	0.1358 gr.	0.1298 gr.	+0.0060 gr.	+4.62
	(5) 0.2095 gr.	0.1340 gr.	0.1298 gr.	+0.0042 gr.	+3.23
	(6) 0.2097 gr.	0.1342 gr.	0.1298 gr.	+0.0044 gr.	+3.39
X.	(7) 0.0420 gr.	0.0269 gr.	0.0265 gr.	+0.0004 gr.	+1.51
	(8) 0.0427 gr.	0.0273 gr.	0.0265 gr.	+0.0008 gr.	+3.02
	(9) 0.0444 gr.	0.0284 gr.	0.0265 gr.	+0.0019 gr.	+7.17
	(10) 0.0448 gr.	0.0286 gr.	0.0265 gr.	+0.0021 gr.	+7.92

Experiments (11) to (16) inclusive were made with portions of 40 cm.<sup>3</sup> each of Solution II. Portions (11) and (12) were acidulated with hydrochloric acid and, after the addition of ammonia in excess, precipitated with 6 cm.<sup>3</sup> of magnesian sulphate mixture. Portions (13) and (14) were acidulated with 0.5 gr. of citric acid and, after the addition of ammonia, treated with 6 cm.<sup>3</sup> of magnesian sulphate mixture; which amount failing (on account of the presence of a citrate) to throw the phosphoric acid down entirely, 6 cm.<sup>3</sup> more of the same mixture were added to complete the precipitation. Portions (15) and (16) were acidulated with hydrochloric acid and 0.5 gr. of citric acid, ammonia added in excess and precipitation effected with 12 cm.<sup>3</sup> of magnesian sulphate mixture. The precipitates of (11), (13), and (15) were filtered off, washed and ignited; those of (12), (14), and (16) were filtered off on paper, drained, dissolved (without previous washing) in hydrochloric acid, thrown down again with ammonia, and, the precipitate having settled, filtered off, after the addition of a few centimeters of magnesian sulphate mixture, upon asbestos, washed and ignited. The precipitates were all thrown down the first time from hot solutions.

	Mg <sub>3</sub> F <sub>2</sub> O <sub>7</sub>	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Percent error.
II.	(11) 0.0811 gr.	0.0519 gr.	0.0512 gr.	+0.0007 gr.	+1.37
	(12) 0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.
	(13) 0.0827 gr.	0.0529 gr.	0.0512 gr.	+0.0017 gr.	+3.31
	(14) 0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.
	(15) 0.0827 gr.	0.0529 gr.	0.0512 gr.	+0.0017 gr.	+3.31
	(16) 0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.

Experiments (17) to (20) inclusive were made with portions of 40 cm.<sup>3</sup> each of Solution III. To each portion were added 6 cm.<sup>3</sup> of strong hydrochloric acid, 20 cm.<sup>3</sup> of strong ammonia, and 20 cm.<sup>3</sup> of magnesian sulphate mixture. The first precipitate was filtered off on paper, drained, dissolved in hydrochloric acid and thrown down again with ammonia. In portions (17) and (18) the second precipitation was effected instantly by adding concentrated ammonia to the acid solution, the precipitate being consequently quite voluminous, and magnesian sulphate mixture was added after settling. In portions (19) and (20) the second precipitation was brought about more gradually by neutralizing with dilute ammonia.



	$Mg_2P_2O_7$	$P_2O_5$ found.	$P_2O_5$ required.	Error.	Per cent. error.
III.	(17) 0.2928 gr.	0.1873 gr.	0.1863 gr.	+0.0010 gr.	+0.54
	(18) 0.2937 gr.	0.1878 gr.	0.1863 gr.	+0.0015 gr.	+0.80
	(19) 0.2923 gr.	0.1869 gr.	0.1863 gr.	+0.0006 gr.	+0.32
	(20) 0.2925 gr.	0.1871 gr.	0.1863 gr.	+0.0008 gr.	+0.43

In experiments (21) to (26) inclusive 40 cm.<sup>3</sup> of magnesian sulphate mixture from which the ammonia had been removed by boiling were in each case added to 40 cm.<sup>3</sup> of the phosphate solution; in (21), (22), (23), and (24) directly, in (25) and (26) after acidifying with 5 cm.<sup>3</sup> of strong hydrochloric acid and then making faintly but distinctly ammoniacal. In every case dilute ammonia was added gradually at first, and 5 cm.<sup>3</sup> of strong ammonia after, the settling of the precipitate. Portions (21) and (22) were precipitated hot.

	$Mg_2P_2O_7$	$P_2O_5$ found.	$P_2O_5$ required.	Error.	Per cent. error.
V.	(21) 0.3112 gr.	0.1991 gr.	0.1875 gr.	+0.0116 gr.	+6.18
	(22) 0.3114 gr.	0.1992 gr.	0.1875 gr.	+0.0117 gr.	+6.24
	(23) 0.3028 gr.	0.1936 gr.	0.1875 gr.	+0.0061 gr.	+3.25
	(24) 0.3048 gr.	0.1949 gr.	0.1875 gr.	+0.0074 gr.	+3.94
VIII.	(25) 0.3469 gr.	0.2219 gr.	0.2142 gr.	+0.0077 gr.	+3.59
	(26) 0.3514 gr.	0.2248 gr.	0.2142 gr.	+0.0106 gr.	+4.94

For experiments (27) to (39) inclusive portions of 40 cm.<sup>3</sup> each of the phosphate solutions were taken. To portions (27) and (28) were added 12 cm.<sup>3</sup> of magnesian chloride mixture; to (29) and (30) 5 cm.<sup>3</sup> of strong hydrochloric acid, strong ammonia to neutralization and 10 cm.<sup>3</sup> beside, and then 12 cm.<sup>3</sup> of magnesian chloride mixture; to portions (31) to (39) inclusive 5 cm.<sup>3</sup> of strong hydrochloric acid, 20 cm.<sup>3</sup> of strong ammonia and 10 cm.<sup>3</sup> of magnesian chloride mixture, 5 cm.<sup>3</sup> more of the same being added, except in experiment (31), after the settling of the precipitate.

	$Mg_2P_2O_7$	$P_2O_5$ found.	$P_2O_5$ required.	Error.	Per cent. error.
VI.	(27) 0.3430 gr.	0.2194 gr.	0.2195 gr.	-0.0001 gr.	-0.04
	(28) 0.3438 gr.	0.2199 gr.	0.2195 gr.	+0.0004 gr.	+0.18
	(29) 0.3425 gr.	0.2191 gr.	0.2195 gr.	-0.0004 gr.	-0.18
	(30) 0.3435 gr.	0.2197 gr.	0.2195 gr.	+0.0002 gr.	+0.09

	$Mg_2P_2O_7$ .	$P_2O_5$ found.	$P_2O_5$ required.	Error.	Per cent. error.
III.	(31)	0.2902 gr.	0.1857 gr.	0.1863 gr.	-0.0006 gr. -0.32
	(32)	0.2903 gr.	0.1857 gr.	0.1863 gr.	-0.0006 gr. -0.32
	(33)	0.2908 gr.	0.1860 gr.	0.1863 gr.	-0.0003 gr. -0.16
	(34)	0.2913 gr.	0.1863 gr.	0.1863 gr.	0. 0.
	(35)	0.2919 gr.	0.1866 gr.	0.1863 gr.	+0.0003 gr. +0.16
	(36)	0.2920 gr.	0.1867 gr.	0.1863 gr.	+0.0004 gr. +0.21
	(37)	0.2920 gr.	0.1867 gr.	0.1863 gr.	+0.0004 gr. +0.21
IV.	(38)	0.2935 gr.	0.1877 gr.	0.1885 gr.	-0.0008 gr. -0.42
	(39)	0.2941 gr.	0.1880 gr.	0.1885 gr.	-0.0005 gr. -0.27

In experiments (40) to (43) inclusive 10 cm.<sup>3</sup> of strong ammonia were added to 40 cm.<sup>3</sup> of the phosphate solution and then 10 cm.<sup>3</sup> of magnesian chloride mixture. The precipitates of (42) and (43) were dissolved by adding hydrochloric acid to the supernatant liquid and thrown down again with ammonia.

	$Mg_2P_2O_7$ .	$P_2O_5$ found.	$P_2O_5$ required.	Error.	Per cent. error.
V.	(40)	0.2946 gr.	0.1884 gr.	0.1875 gr.	+0.0009 gr. +0.48
	(41)	0.2950 gr.	0.1887 gr.	0.1875 gr.	+0.0012 gr. +0.64
	(42)	0.2927 gr.	0.1872 gr.	0.1875 gr.	-0.0003 gr. -0.16
	(43)	0.2936 gr.	0.1878 gr.	0.1875 gr.	+0.0003 gr. +0.16

In experiments (44) to (47) inclusive 10 cm.<sup>3</sup> of strong ammonia were added to 40 cm.<sup>3</sup> of the phosphate solution, and then 25 cm.<sup>3</sup> of magnesian chloride. The precipitates of (46) and (47) were dissolved by hydrochloric acid added to the supernatant liquid and again thrown down with ammonia.

	$Mg_2P_2O_7$ .	$P_2O_5$ found.	$P_2O_5$ required.	Error.	Per cent. error.
IV.	(44)	0.2977 gr.	0.1904 gr.	0.1885 gr.	+0.0019 gr. +1.01
	(45)	0.2986 gr.	0.1910 gr.	0.1885 gr.	+0.0025 gr. +1.33
	(46)	0.2952 gr.	0.1888 gr.	0.1885 gr.	+0.0003 gr. +0.16
	(47)	0.2954 gr.	0.1889 gr.	0.1885 gr.	+0.0004 gr. +0.21

For each of the experiments (48) to (60) inclusive 40 cm.<sup>3</sup> of the phosphate solution were taken. Portions (48), (49), (50), and (51) were precipitated with 40 cm.<sup>3</sup> of magnesian chloride mixture containing 4 gr. of ammoniac chloride more than the usual amount, the precipitate being added to the phosphate in experiments (48) and (49), the phosphate (gradually) to the precipitant in (50) and (51). In experiments (52) and (53) the solution of the phosphate was acidulated with 8 cm.<sup>3</sup> of hydrochloric acid, made alkaline with ammonia—

about 4 gr. of ammoniac chloride being produced in the process— and precipitated with 40 cm.<sup>3</sup> of magnesian chloride mixture. In experiments (54) to (60) inclusive 40 cm.<sup>3</sup> of magnesian chloride mixture from which the ammonia had been expelled by boiling were added to the phosphate solution—in experiments (56), (57), (58), (59), and (60) directly, in (54) and (55) after adding enough ammonia to make the solution smell distinctly of it—and ammonia afterward strong in (57), (58), (59), and (60), but dilute at first in (54), (55), and (56) and strong after the settling of the precipitate. Solutions (59) and (60) were precipitated hot.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
VII.	(48)	0.2880 gr.	0.1842 gr.	0.1831 gr.	+0.0011 gr.	+0.60
	(49)	0.2881 gr.	0.1843 gr.	0.1831 gr.	+0.0012 gr.	+0.66
	(50)	0.2886 gr.	0.1846 gr.	0.1831 gr.	+0.0015 gr.	+0.82
	(51)	0.2888 gr.	0.1847 gr.	0.1831 gr.	+0.0016 gr.	+0.87
	(52)	0.2882 gr.	0.1844 gr.	0.1831 gr.	+0.0013 gr.	+0.71
	(53)	0.2882 gr.	0.1844 gr.	0.1831 gr.	+0.0013 gr.	+0.71
	(54)	0.2865 gr.	0.1832 gr.	0.1831 gr.	+0.0001 gr.	+0.05
	(55)	0.2870 gr.	0.1835 gr.	0.1831 gr.	+0.0004 gr.	+0.22
V.	(56)	0.2931 gr.	0.1875 gr.	0.1875 gr.	0.	0.
	(57)	0.2940 gr.	0.1880 gr.	0.1875 gr.	+0.0005 gr.	+0.27
	(58)	0.2950 gr.	0.1887 gr.	0.1875 gr.	+0.0012 gr.	+0.64
	(59)	0.2983 gr.	0.1907 gr.	0.1875 gr.	+0.0032 gr.	+1.70
	(60)	0.3017 gr.	0.1930 gr.	0.1875 gr.	+0.0055 gr.	+2.93

In experiments (61) to (66) inclusive 5 cm.<sup>3</sup> of strong hydrochloric acid were added to 40 cm.<sup>3</sup> of the phosphate solution and then ammonia in slight excess. Portions (61), (62), (63), and (64) were precipitated with 20 cm.<sup>3</sup> of magnesian chloride mixture. To (65) and (66) were added 20 cm.<sup>3</sup> of magnesian chloride mixture from which the ammonia had been expelled, and afterward ammonia dilute at the first and strong after the precipitate had settled. Solutions (63), (64), (65), and (66) contained previous to precipitating 3 gr. of sodic chloride each.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
XVI.	(61)	0.0426 gr.	0.0272 gr.	0.0269 gr.	+0.0003 gr.	+1.11
	(62)	0.0427 gr.	0.0273 gr.	0.0269 gr.	+0.0004 gr.	+1.49
	(63)	0.0430 gr.	0.0275 gr.	0.0269 gr.	+0.0006 gr.	+2.23
	(64)	0.0431 gr.	0.0276 gr.	0.0269 gr.	+0.0007 gr.	+2.60
	(65)	0.0426 gr.	0.0272 gr.	0.0269 gr.	+0.0003 gr.	+1.11
	(66)	0.0426 gr.	0.0272 gr.	0.0269 gr.	+0.0003 gr.	+1.11

## PHOSPHOTUNGSTATES.

In each of the following experiments upon the determination of phosphoric oxide in phosphotungstates 1 gr. of crystallized normal sodic tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) was dissolved and added to 40 cm.<sup>3</sup> of a phosphate solution, the phosphotungstate produced by the addition of acid in measured amount or until the yellow color of the solution indicated its formation, and ammonia added until the precipitate first formed redissolved.

In experiments (67) to (76) inclusive there were added to each portion containing the phosphate and tungstate 0.5 gr. of citric acid, hydrochloric acid until the solution became yellow, ammonia until it gave its odor distinctly to the solution, and then 20 cm.<sup>3</sup> of magnesian sulphate mixture. Portions (75) to (79) inclusive were treated in a similar manner, excepting that 5 cm.<sup>3</sup> of strong hydrochloric acid and no citric acid were added to them. The precipitates of (67), (68), (69), and (70) were filtered off on asbestos, washed, and ignited in the manner previously described. The precipitates of (71), (72), (73), and (74) were filtered off on paper, washed with magnesian sulphate mixture, and then with a few centimeters of ammonia, dissolved in hydrochloric acid and reprecipitated with ammonia, a few centimeters of magnesian sulphate mixture being added after the precipitate had settled. The precipitates of (75) to (79) inclusive were filtered off on paper, washed with magnesian sulphate mixture, dissolved in hydrochloric acid and thrown down again with ammonia, a few centimeters of magnesian sulphate being added after the settling of the precipitate. The second precipitates were filtered off on asbestos, washed, and ignited as usual.

	$\text{Mg}_3\text{P}_2\text{O}_7$	$\text{P}_2\text{O}_5$ found.	$\text{P}_2\text{O}_5$ required.	Error.	Per cent. error.
X.	(67)	0.0439 gr.	0.0281 gr.	0.0265 gr.	+0.0016 gr. +6.04
	(68)	0.0445 gr.	0.0285 gr.	0.0265 gr.	+0.0020 gr. +7.55
	(69)	0.0448 gr.	0.0286 gr.	0.0265 gr.	+0.0021 gr. +7.92
	(70)	0.0455 gr.	0.0291 gr.	0.0265 gr.	+0.0026 gr. +9.81
	(71)	0.0388 gr.	0.0248 gr.	0.0265 gr.	-0.0017 gr. -6.41
	(72)	0.0390 gr.	0.0249 gr.	0.0265 gr.	-0.0016 gr. -6.04
	(73)	0.0391 gr.	0.0250 gr.	0.0265 gr.	-0.0015 gr. -5.66
	(74)	0.0394 gr.	0.0252 gr.	0.0265 gr.	-0.0013 gr. -4.90
	(75)	0.0421 gr.	0.0269 gr.	0.0265 gr.	+0.0004 gr. +1.51
	(76)	0.0426 gr.	0.0272 gr.	0.0265 gr.	+0.0007 gr. +2.64
XIII.	(77)	0.0424 gr.	0.0271 gr.	0.0270 gr.	+0.0001 gr. +0.37
	(78)	0.0427 gr.	0.0273 gr.	0.0270 gr.	+0.0003 gr. +1.11
	(79)	0.0428 gr.	0.0274 gr.	0.0270 gr.	+0.0004 gr. +1.48

In experiments (80) to (82) and (85) to (88) inclusive there were added to each portion containing the phosphate and tungstate 0.5 gr. of citric acid, hydrochloric acid until the solution became yellow, ammonia in excess and 20 cm.<sup>3</sup> of magnesian chloride mixture; in experiments (83) and (84), and (89) to (91) inclusive, 5 cm.<sup>3</sup> of strong hydrochloric acid (with no citric acid), ammonia in excess and 20 cm.<sup>3</sup> of magnesian chloride mixture. The precipitates of (85) to (91) inclusive were filtered off on paper, washed with magnesian chloride mixture, dissolved in hydrochloric acid and thrown down again with ammonia. The first precipitates of experiments (80) to (84) and the second precipitates of portions (85) to (91) were collected on asbestos, washed, and ignited as usual.

	$Mg_2P_2O_7$ .	$P_2O_5$ found.	$P_2O_5$ required.	Error.	Per cent error.
XI.	(80) 0.0454 gr.	0.0290 gr.	0.0266 gr.	+0.0024 gr.	+ 9.02
	(81) 0.0464 gr.	0.0297 gr.	0.0266 gr.	+0.0031 gr.	+11.65
	(82) 0.0466 gr.	0.0298 gr.	0.0266 gr.	+0.0032 gr.	+12.03
XVI.	(83) 0.0444 gr.	0.0284 gr.	0.0269 gr.	+0.0015 gr.	+ 5.58
	(84) 0.0447 gr.	0.0286 gr.	0.0269 gr.	+0.0017 gr.	+ 6.32
XII.	(85) 0.0405 gr.	0.0256 gr.	0.0270 gr.	—0.0014 gr.	— 5.18
	(86) 0.0414 gr.	0.0265 gr.	0.0270 gr.	—0.0005 gr.	— 1.85
	(87) 0.0414 gr.	0.0265 gr.	0.0270 gr.	—0.0005 gr.	— 1.85
	(88) 0.0416 gr.	0.0266 gr.	0.0270 gr.	—0.0004 gr.	— 1.48
XIII.	(89) 0.0423 gr.	0.0270 gr.	0.0270 gr.	0.	0.
	(90) 0.0424 gr.	0.0271 gr.	0.0270 gr.	+0.0001 gr.	+ 0.37
	(91) 0.0430 gr.	0.0275 gr.	0.0270 gr.	+0.0005 gr.	+ 1.85

In experiments (92) to (101) inclusive 5 cm.<sup>3</sup> of strong hydrochloric acid were added to each portion containing the phosphate and tungstate, ammonia in distinct excess, magnesian chloride mixture — in (92), (93), (94), and (95) 1.5 cm.<sup>3</sup> and 1.5 cm.<sup>3</sup> more after the precipitate had settled; in (96) and (97) 2 cm.<sup>3</sup>; in (98) and (99) 5 cm.<sup>3</sup>; in (100) and (101) 10 cm.<sup>3</sup> drop by drop and then 10 cm.<sup>3</sup> more at once, — and finally after the precipitate had settled, ammonia until the solution evolved a strong ammoniacal odor.

	$Mg_2P_2O_7$ .	$P_2O_5$ found.	$P_2O_5$ required.	Error.	Per cent error.
XIV.	(92) 0.0424 gr.	0.0271 gr.	0.0269 gr.	+0.0002 gr.	+0.74
	(93) 0.0427 gr.	0.0273 gr.	0.0269 gr.	+0.0004 gr.	+1.49
XV.	(94) 0.0428 gr.	0.0274 gr.	0.0269 gr.	+0.0005 gr.	+1.86
	(95) 0.0429 gr.	0.0274 gr.	0.0269 gr.	+0.0005 gr.	+1.86

		$Mg_2P_2O_7$	$P_2O_5$ found.	$P_2O_5$ required.	Error.	Per cent. error.
XIV.	{ (96)	0.0430 gr.	0.0275 gr.	0.0269 gr.	+0.0006 gr.	+2.23
	{ (97)	0.0431 gr.	0.0276 gr.	0.0269 gr.	+0.0007 gr.	+2.60
	{ (98)	0.0436 gr.	0.0279 gr.	0.0269 gr.	+0.0010 gr.	+3.72
	{ (99)	0.0440 gr.	0.0281 gr.	0.0269 gr.	+0.0012 gr.	+4.46
XV.	{ (100)	0.0441 gr.	0.0282 gr.	0.0269 gr.	+0.0013 gr.	+4.83
	{ (101)	0.0447 gr.	0.0286 gr.	0.0269 gr.	+0.0017 gr.	+6.32

In experiments (102) to (115) inclusive, 5 cm.<sup>3</sup> of strong hydrochloric acid were added to each portion of phosphate and tungstate, and to portions (112), (113), (114), and (115) 0.5 gr. of citric acid; to every portion, excepting (108) and (109), ammonia in distinct excess; to (108) and (109) ammonia until the precipitate which formed at first was redissolved but not until the solution smelled of ammonia; to all, individually, 20 cm.<sup>3</sup> of magnesian chloride mixture from which the ammonia had been expelled, and, after the settling of the precipitate, ammonia in strong excess.

		$Mg_2P_2O_7$	$P_2O_5$ found.	$P_2O_5$ required.	Error.	Per cent. error.
XV.	{ (102)	0.0436 gr.	0.0279 gr.	0.0269 gr.	+0.0010 gr.	+3.72
	{ (103)	0.0441 gr.	0.0282 gr.	0.0269 gr.	+0.0013 gr.	+4.83
XVI.	{ (104)	0.0446 gr.	0.0285 gr.	0.0269 gr.	+0.0016 gr.	+5.95
	{ (105)	0.0454 gr.	0.0290 gr.	0.0269 gr.	+0.0021 gr.	+7.80
	{ (106)	0.0459 gr.	0.0294 gr.	0.0269 gr.	+0.0025 gr.	+9.29
	{ (107)	0.0465 gr.	0.0297 gr.	0.0269 gr.	+0.0025 gr.	+9.29
XV.	{ (108)	0.0498 gr.	0.0318 gr.	0.0269 gr.	+0.0049 gr.	+18.21
	{ (109)	0.0543 gr.	0.0347 gr.	0.0269 gr.	+0.0078 gr.	+28.99
IX.	{ (110)	0.3251 gr.	0.2079 gr.	0.2017 gr.	+0.0062 gr.	+3.04
	{ (111)	0.3262 gr.	0.2086 gr.	0.2017 gr.	+0.0069 gr.	+3.39
	{ (112)	0.3381 gr.	0.2178 gr.	0.2017 gr.	+0.0161 gr.	+7.91
	{ (113)	0.3398 gr.	0.2187 gr.	0.2017 gr.	+0.0170 gr.	+8.35
	{ (114)	0.3423 gr.	0.2190 gr.	0.2017 gr.	+0.0173 gr.	+8.49
	{ (115)	0.3429 gr.	0.2193 gr.	0.2017 gr.	+0.0176 gr.	+8.64

#### PHOSPHOMOLYBDATES.

In each of the following experiments upon the determination of phosphoric oxide in phosphomolybdates, 0.5 gr. of molybdic oxide ( $MO_3$ ) were dissolved in ammonia and added to 40 cm.<sup>3</sup> of a phosphate solution, 5 cm.<sup>3</sup> of strong hydrochloric acid added and ammonia

in distinct excess. To portions (116) to (120) inclusive were added 20 cm.<sup>3</sup> of magnesian chloride mixture, and to portions (121) and (122) 20 cm.<sup>3</sup> of magnesian sulphate mixture. The first precipitates of (119), (120), (121), and (122) were filtered off on paper, dissolved in hydrochloric acid and thrown down again with ammonia, collected on asbestos (as the first precipitates of the other portions were), washed and ignited as usual. Portions (123) and (124) were precipitated with 1.5 cm.<sup>3</sup> of magnesian chloride mixture, 1.5 cm.<sup>3</sup> being added after the precipitate had settled, together with ammonia in strong excess. Portions (125) to (129) inclusive were precipitated with 20 cm.<sup>3</sup> of magnesian chloride mixture from which the ammonia had been expelled, and ammonia was added in strong excess after the settling of the precipitate.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
XII.	{ (116)	0.0441 gr.	0.0282 gr.	0.0270 gr.	+0.0012 gr.	+4.44
	{ (117)	0.0452 gr.	0.0289 gr.	0.0270 gr.	+0.0019 gr.	+7.04
	{ (118)	0.0458 gr.	0.0293 gr.	0.0270 gr.	+0.0023 gr.	+8.52
XIII.	{ (119)	0.0423 gr.	0.0271 gr.	0.0270 gr.	+0.0001 gr.	+0.37
	{ (120)	0.0425 gr.	0.0272 gr.	0.0270 gr.	+0.0002 gr.	+0.74
	{ (121)	0.0423 gr.	0.0271 gr.	0.0270 gr.	+0.0001 gr.	+0.37
	{ (122)	0.0427 gr.	0.0273 gr.	0.0270 gr.	+0.0003 gr.	+1.11
XVI.	{ (123)	0.0423 gr.	0.0270 gr.	0.0269 gr.	+0.0001 gr.	+0.37
	{ (124)	0.0424 gr.	0.0271 gr.	0.0269 gr.	+0.0002 gr.	+0.74
	{ (125)	0.0424 gr.	0.0271 gr.	0.0269 gr.	+0.0002 gr.	+0.74
	{ (126)	0.0425 gr.	0.0272 gr.	0.0269 gr.	+0.0003 gr.	+1.11
IX.	{ (127)	0.3168 gr.	0.2026 gr.	0.2017 gr.	+0.0009 gr.	+0.44
	{ (128)	0.3173 gr.	0.2030 gr.	0.2017 gr.	+0.0013 gr.	+0.64
	{ (129)	0.3180 gr.	0.2033 gr.	0.2015 gr.	+0.0016 gr.	+0.79

Experiments (1) to (10) inclusive, (11), (13), and (15) demonstrate that the method of estimating the phosphoric oxide of alkaline phosphates by precipitation with magnesian sulphate mixture and washing until the chlorine reaction vanishes from the filtrate gives results far too high when the amount of the precipitant used is in any considerable excess of the amount theoretically required. Thus, in experiments (1) to (6), in each of which 20 cm.<sup>3</sup> of magnesian sulphate mixture were used, the amount required by theory being about 5.2 cm.<sup>3</sup>, the error varies from +0.0033 gr. to +0.0060 gr. on 0.1298 gr. of phosphoric oxide, or from +2.54 to +3.39 per cent.; in experi-

ments (7) to (10), in each of which 20 cm.<sup>3</sup> of the precipitant were used, while theory requires about 1.1 cm.<sup>3</sup>, the error upon 0.0265 gr. of phosphoric oxide varies from +0.0004 gr. to +0.0021 gr., or from +1.51 to +7.92 per cent.; in experiment (11) in which 6 cm.<sup>3</sup> of the precipitant were used, while about 2.1 cm.<sup>3</sup> were theoretically required, the error is +0.0007 gr. upon 0.0512 gr. of phosphoric oxide, or +1.37 per cent.; and in experiments (13) and (15) in which 12 cm.<sup>3</sup> of the precipitant were used, while about 2.1 cm.<sup>3</sup> were theoretically required, the error upon 0.0512 gr. of phosphoric oxide was +0.0017 gr., or +3.31 per cent.

Experiments (21) to (26) inclusive show that when the process was varied so as to precipitate the phosphate solution, either containing no free ammonia or a very small quantity, by a magnesian sulphate mixture from which the ammonia had been expelled, the error of the result varied from +0.0061 gr. to +0.0117 gr. upon 0.1875 gr. of phosphoric oxide, or from +3.25 to +6.24 per cent.; and from +0.0077 gr. to +0.0106 gr. upon 0.2142 gr. of phosphoric oxide, or from +3.59 to +4.94 per cent., — the greatest errors appearing naturally in the experiments made with hot solutions containing no free ammonia, in which cases the hydro-magnesian phosphate first thrown down was partially changed into tri-magnesian phosphate by the action of the heat, and therefore not converted into ammonio-magnesian phosphate upon the subsequent addition of ammonia.

Experiments (12), (14), (16), and (17) to (20) inclusive indicate that tolerably good results may be obtained by draining the first precipitate, dissolving in hydrochloric acid and reprecipitating with ammonia; the first three experiments showing incidentally that the addition of small amounts of citric acid does not prevent precipitation to any very marked degree in presence of a considerable excess — in this case about 10 cm.<sup>3</sup> to 0.5 gr. of citric acid — of magnesian sulphate mixture. Thus in experiments (12), (14), and (16) the error was 0; and in experiments (17) to (20) the error varied from +0.0006 gr. to +0.0015 gr. on 0.1863 gr. of phosphoric oxide, or from +0.32 to +0.80 per cent., the mean error being about +0.0006 gr., or +0.32 per cent.

It appears from these experiments that the method of precipitating by magnesian sulphate mixture without the solution and second precipitation ought to give an accurate determination of phosphoric acid, providing only that the amount of the precipitant used were just sufficient to complete the precipitation. But this condition renders the process practically useless in ordinary cases; and inasmuch as in



Kissel's method of compensating for enclosed material by excessive washing, the amount of washing must necessarily be proportioned both to the weight of phosphoric acid present and to the excess of the precipitant, — elements which introduce a great deal of uncertainty, — it would appear that if magnesian sulphate mixture is to be the precipitant the method of precipitating twice is the only one which can be relied upon on all occasions to give tolerably correct results.

The results obtained in experiments (27) to (66) by precipitating with magnesian chloride mixture are different as the method of treatment varies. It will be noticed that in experiments otherwise essentially similar the variations in the amount of the precipitant produce differences in the results. Thus, in experiments (27) to (43), in which 10 cm.<sup>3</sup> or 12 cm.<sup>3</sup> of the precipitant were used, the error varies from  $-0.0008$  gr. to  $+0.0012$  gr., or from  $-0.42$  to  $+0.64$  per cent., the mean error being nearly 0; while in the experiments (48) to (53) in which 40 cm.<sup>3</sup> of the precipitant were used, the error varies from  $+0.0011$  gr. to  $+0.0016$  gr., or from  $+0.60$  to  $+0.87$  per cent., the mean error being about  $+0.0013$  gr., or  $+0.71$  per cent. It will be seen also that while it makes no apparent difference whether the precipitant is added to the phosphate directly, as in (27) and (28), or after treatment with hydrochloric acid, as in (29) to (39), the dissolving of a precipitate, by adding hydrochloric acid to the supernatant liquid, and reprecipitation with ammonia tend to reduce the results below those of experiments in which this has not been done, but which are similar in other respects. This appears very distinctly in a comparison of experiments (40) and (41) with (42) and (43), where the mean error is reduced from about  $+0.0010$  gr. upon 0.1875 gr. of phosphoric oxide, or from  $+0.56$  per cent., to 0; or of experiments (44) and (45) with (46) and (47), where the mean error is reduced from  $+0.0022$  gr. to about  $+0.0003$  gr. upon 0.1885 gr. of phosphoric oxide, or from  $+1.17$  to  $+0.18$  per cent.

It appears, further, from a comparison of experiments (54) to (58) with experiments (48) to (53), that results got by precipitating solutions containing either no free ammonia, as in (56), (57) and (58), or only a small amount, as in (54) and (55), by a magnesian chloride mixture deprived of ammonia are more nearly correct than those got by precipitating under essentially similar conditions with the ammoniacal magnesian chloride mixture as in (48) to (53). Thus, in (48) to (53) the error varies from  $+0.0011$  gr. to  $+0.0016$  gr. upon 0.1831 gr. of phosphoric oxide, or from  $+0.60$  to  $+0.87$  per cent.,

the mean error being about  $+0.0013$  gr. or  $+0.71$  per cent.; while in (54) to (58) the error varies from 0 to  $+0.0012$  gr. upon 0.1831 gr. or 0.1875 gr. of phosphoric oxide, or from 0 to  $+0.64$  per cent., the mean error being about  $+0.0004$  gr. or  $+0.22$  per cent.; and it is to be remarked that in (54), (55) and (56), in which dilute ammonia was added after the non-ammoniacal magnesian chloride mixture, the mean error — about  $+0.0002$  gr. or  $+0.10$  per cent. — is much smaller than the mean error of (57) and (58) — about  $+0.0008$  gr., or  $+0.44$  per cent. — in which strong ammonia was added after the non-ammoniacal magnesian chloride mixture. The high results of experiments (59) and (60), in which the non-ammoniacal magnesian chloride mixture was added to the hot phosphate solution, are explained by the fact that a part of the hydromagnesian phosphate first formed was decomposed by the heat with the formation of trimagnesian phosphate, and therefore not completely converted into ammonio-magnesian phosphate by the ammonia subsequently added. From experiments (61) to (64) it will be seen that the presence of 3 gr. of sodic chloride in the phosphate solution raises the figures of the analysis materially when precipitation is effected by the ammoniacal magnesian chloride mixture, even with small weights of phosphoric oxide, and that better results are got in (65) and (66) by using the non-ammoniacal mixture.

The use of an excessive quantity, too, of ammoniac chloride tends apparently to reduce the error. Thus, in experiments (48) to (53) the mean error was about  $+0.0013$ , gr., or  $+0.71$  per cent., while in (44) and (45), in which free ammonia, but no ammoniac chloride beyond the amount in the magnesian chloride mixture, was used, the mean error is  $+0.0022$  or  $+1.17$  per cent., although less of the precipitant was used in the latter.

The cause of all these differences in the accuracy of the determination of the phosphoric oxide of alkali phosphates by precipitation with magnesian chloride mixture seems to lie in the variations of the rapidity with which the ammonio-magnesian phosphate is crystallized from solution. The sudden addition of a large amount of the precipitant, or of an excess of the precipitant to a strongly ammoniacal solution of the phosphate, or of strong ammonia to a solution of the precipitate in acid, tends to hasten the deposition, and so to prevent the complete exclusion of foreign material from the crystalline structure; while in the precipitation of solutions containing large amounts of ammoniac chloride, or of weakly ammoniacal solutions, or of solutions of the precipitate in acid, by the gradual addition of ammonia the process of crystallization goes on more slowly and perfectly.

The differences between results got by using a magnesian sulphate mixture and those obtained with a magnesian chloride mixture may be, perhaps, partly explained by the supposition that magnesian sulphate resists exclusion during the crystallization of the ammonio-magnesian phosphate more effectively than magnesian chloride, and partly by the fact that magnesian sulphate enclosed in a precipitate would probably not change materially in composition during an ignition over a Bunsen burner in a crucible standing on platinum foil, while magnesian chloride ignited in presence of aqueous vapor under like circumstances would be converted into magnesian oxide whose molecular weight is but one-third of that of the sulphate. It is difficult, at all events, to conceive how the contamination of the precipitate can be other than mechanical; for the trimagnesian phosphate could only be produced by a reaction between the ammonio-magnesian phosphate and magnesian sulphate, — which is quite improbable, at least in the cold, — and the formation of a magnesian hydrate or basic sulphate would seem to be altogether unlikely under the circumstances.

In the experiments upon the phosphotungstates the mean error of the method involving a single precipitation with magnesian sulphate mixture (experiments 67 to 70) was about  $+0.0021$  gr. upon  $0.0265$  gr. and with magnesian chloride mixture (experiments 80 to 84) about  $+0.0024$  gr., upon  $0.0266$  gr. or  $0.0269$  gr., of phosphoric oxide, or about  $+8.44$  per cent. The mean error of the method of double precipitation upon nearly the same amounts of phosphoric oxide, the precipitant alone being used to wash the first precipitate and no citrate being present, was, with magnesian sulphate mixture (experiments 75 to 79) about  $+0.0004$  gr., or  $+1.51$  per cent., and with magnesian chloride mixture (experiments 89 to 91)  $+0.0002$  gr., or  $+0.74$  per cent.; the mean error when the first precipitate by magnesian sulphate mixture was washed with the precipitant and afterwards with ammonia water (experiments 71 to 74) being about  $-0.0015$  gr., or  $-5.66$  per cent.; and when the first precipitate was thrown down in presence of a citrate by magnesian chloride mixture and washed with the precipitant (experiments 85 to 88), about  $-0.0007$  gr., or  $-2.59$  per cent. When precipitation was effected with  $1.5$  cm.<sup>3</sup> of magnesian chloride mixture, the same being added after precipitation (experiments 92 to 95) the mean error upon  $0.0269$  gr. of phosphoric oxide was  $+0.0004$  gr. or  $+1.49$  per cent.; when by  $2$  cm.<sup>3</sup> (experiments 96 and 97) about  $+0.0006$  gr., or  $+2.23$  per cent.; when by  $5$  cm.<sup>3</sup> (experiments 98 and 99)  $+0.0011$  gr., or  $+4.09$  per

cent.; and when by 10 cm.<sup>3</sup> added drop by drop, with 10 cm.<sup>3</sup> more subsequent to precipitation (experiments 100 and 101)  $+0.0015$  gr., or  $+5.58$  per cent. The mean error of the determination by precipitating with 20 cm.<sup>3</sup> of non-ammoniacal magnesian chloride mixture, in slightly ammoniacal solutions (experiments 102 to 107 and 110 to 115) was about  $+0.0018$  gr. upon 0.0269 gr. of phosphoric oxide, or  $+6.69$  per cent.; about  $+0.0065$  gr. upon 0.2017 gr. of phosphoric oxide, or  $+3.22$  per cent., in solutions containing no citrate, and in solutions containing a citrate  $+0.0170$  gr., or  $+8.35$  per cent. The mean error when 20 cm.<sup>3</sup> of non-ammoniacal magnesian chloride mixture was added to the solution of phosphate and tungstate containing no free ammonia (experiments 108 and 109) amounted to about  $+0.0063$  gr. upon 0.0269 gr. of phosphoric oxide, or  $+23.60$  per cent.

The use of citric acid in many of the experiments above, in accordance with a suggestion of Dr. Gibbs, appears to be attended with unfavorable results. Thus in experiments (85) to (88), in which the first precipitates were dissolved and reprecipitated, this appears to have lowered the results below those of (89) to (91); while in experiments (80) to (82) and in experiments (112) to (115), in which the first precipitate was not dissolved, it appears to have raised the results above those of (83) and (84), and (110) and (111) respectively, — facts which are perhaps to be explained by attributing to the citrate both a solvent and contaminating action upon the precipitate.

Of the experiments upon the phosphomolybdates (123) and (124), in which the precipitation was effected by 1.5 cm.<sup>3</sup> of magnesian chloride mixture, 1.5 cm.<sup>3</sup> of the same being added afterward, show a mean error of less than  $+0.0002$  gr. upon 0.0269 gr. of phosphoric oxide, or  $+0.55$  per cent.; and experiments (116) to (118) in which 20 cm.<sup>3</sup> of the same precipitant were employed  $+0.0018$  gr. upon 0.0270 gr. of phosphoric oxide, or  $+6.66$  per cent.; experiments (119) to (122), in two of which the precipitation was effected by magnesian sulphate mixture and in two by magnesian chloride mixture, the first precipitate being washed with the precipitant, dissolved in hydrochloric acid and again thrown down, less than  $+0.0002$  gr. upon 0.0270 gr. of phosphoric oxide, or  $+0.65$  per cent. In experiments (125) to (129) in which 20 cm.<sup>3</sup> of the magnesian chloride mixture deprived of ammonia were added to slightly ammoniacal solutions, the mean error was less than  $+0.0003$  gr. on 0.0269 gr. of phosphoric oxide, or  $+0.92$  per cent., and less than  $+0.0013$  gr. on 0.2017 gr. of phosphoric oxide, or  $+0.62$  per cent.

It will be noticed that in the experiments with phosphates and phosphomolybdates a large excess of the magnesian chloride mixture was not markedly prejudicial to the accuracy of results when precautions were taken to induce a slow formation of the precipitate, while in the experiments with phosphotungstates the reverse was true. The reason for this exceptionally unfavorable action in the case of the phosphotungstates is probably indicated in the facts that the addition of free ammonia beyond a certain amount to the solution of a phosphotungstate produces turbidity, and that the addition of magnesia mixture to a clear solution of normal sodic tungstate, ammoniac chloride and ammonia renders the solution opalescent and occasions the deposition, after some hours, of an almost invisible precipitate; but it is to be noted in this connection that the action of magnesia mixture upon a clear ammoniacal solution of ammoniac molybdate and ammoniac chloride is similar to its action upon the tungstate solution.

#### SUMMARY.

It would appear from the preceding account that in determining the phosphoric oxide of alkaline phosphates, free from sulphates or other substances likely to contaminate a precipitate, accuracy is most conveniently and surely attained by adding to the somewhat dilute solution of the phosphate ammonia in slight but quite distinct excess, then an excess of magnesian chloride mixture containing no free ammonia (made by dissolving three parts of crystallized magnesian chloride and eight parts of ammoniac chloride in water, adding water containing ammonia until the volume of the solution reaches forty-eight parts, filtering and boiling off the free ammonia), and, after the precipitate has settled, ammonia until the liquid evolves a strong odor of it. In determining the phosphoric oxide of phosphotungstates the best results are to be got by adding to the solution containing free ammonia an excess of either of the magnesia mixtures, washing the precipitate with the precipitant, dissolving in hydrochloric acid, diluting if necessary and reprecipitating with a little dilute ammonia, adding strong ammonia after the precipitate has settled; or, when working with small amounts, by proceeding as in the case of the phosphates, taking special care, however, that the solution is distinctly ammoniacal before precipitating, and that no great excess of the precipitant is used. In the determination of the phosphoric oxide of phosphomolybdates, the method recommended for use in the case of the phosphates serves very well when the amount of phosphoric oxide

does not exceed (let us say) 0.05 gr., but for amounts larger than this the method of double precipitation recommended for the phosphotungstates is more accurate.

As to the time which should be allowed to pass between precipitating and filtering, my experiments support those of Abesser, Jani, and Märcker\* in pointing to the conclusion that a precipitate may be filtered with safety as soon as it has completely subsided, or, after ten or fifteen minutes.

The use, for the filtration and ignition of the precipitate, of the method which I have employed in the experiments described above greatly expedites the analysis. Thus, with two perforated crucibles at my disposal, I have completed within four and one-half hours from the measuring out of the first solution seven determinations of the phosphoric oxide of an alkaline phosphate, — the ignition of each precipitate requiring less than five minutes.

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\* Zeitschrift für Anal. Chem. XII. 250.

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## V.

ON THE MECHANICAL EQUIVALENT OF HEAT, WITH SUBSIDIARY RESEARCHES ON THE VARIATION OF THE MERCURIAL FROM THE AIR THERMOMETER, AND ON THE VARIATION OF THE SPECIFIC HEAT OF WATER.

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Presented June 11th, 1879.

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## I.—INTRODUCTORY REMARKS.

AMONG the more important constants of nature, the ratio of the heat unit to the unit of mechanical work stands forth prominent, and is used almost daily by the physicist. Yet, when we come to consider

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\* This research was originally to have been performed in connection with Professor Pickering, but the plan was frustrated by the great distance between our residences. An appropriation for this experiment was made by the American Academy of Arts and Sciences at Boston, from the fund which was instituted by Count Rumford, and liberal aid was also given by the Trustees of the Johns Hopkins University, who are desirous, as far as they can, to promote original scientific investigation.

the history of the subject carefully, we find that the only experimenter who has made the determination with anything like the accuracy demanded by modern science, and by a method capable of giving good results, is Joule, whose determination of thirty years ago, confirmed by some recent results, to-day stands almost, if not quite, alone among accurate results on the subject.

But Joule experimented on water of one temperature only, and did not reduce his results to the air thermometer; so that we are still left in doubt, even to the extent of one per cent, as to the value of the equivalent on the air thermometer.

The reduction of the mercurial to the air thermometer, and thence to the absolute scale, has generally been neglected between  $0^{\circ}$  and  $100^{\circ}$  by most physicists, though it is known that they differ several tenths of a degree at the  $45^{\circ}$  point. In calorimetric researches this may produce an error of over one, and even approaching two per cent, especially when a Geissler thermometer is used, which is the worst in this respect of any that I have experimented on; and small intervals on the mercurial thermometers differ among themselves more than one per cent from the difference of the glass used in them.

Again, as water is necessarily the liquid used in calorimeters, its variation of specific heat with the temperature is a very important factor in the determination of the equivalent. Strange as it may appear, we may be said to know almost nothing about the variation of the specific heat of water with the temperature between  $0^{\circ}$  and  $100^{\circ}$  C.

Regnault experimented only above  $100^{\circ}$  C. The experiments of Hirn, and of Jamin and Amaury, are absurd, from the amount of variation which they give. Pfaundler and Plattner confined themselves to points between  $0^{\circ}$  and  $13^{\circ}$ . Münchhausen seems to have made the best experiments, but they must be rejected because he did not reduce to the air thermometer.

In the present series of researches, I have sought, firstly, a method of measuring temperatures on the perfect gas thermometer with an accuracy scarcely hitherto attempted, and to this end have made an extended study of the deviation of ordinary thermometers from the air thermometer; and, secondly, I have sought a method of determining the mechanical equivalent of heat so accurate, and of so extended a range, that the variation of the specific heat of water should follow from the experiments alone.

As to whether or not these have been accomplished, the following pages will show. The curious result that the specific heat of water



on the *air* thermometer decreases from  $0^{\circ}$  to about  $30^{\circ}$  or  $35^{\circ}$ , after which it *increases*, seems to be an entirely unique fact in nature, seeing that there is apparently no other substance hitherto experimented upon whose specific heat *decreases* on rise of temperature without change of state. From a thermodynamic point of view, however, it is of the same nature as the decrease of specific heat which takes place after the vaporization of a liquid.

The close agreement of my result at  $15^{\circ}.7$  C. with the old result of Joule, after approximately reducing his to the air thermometer and latitude of Baltimore, and correcting the specific heat of copper, is very satisfactory to us both, as the difference is not greater than 1 in 400, and is probably less.

I hope at some future time to make a comparison with Joule's thermometers, when the difference can be accurately stated.

## II. — THERMOMETRY.

### (a.) General View.

The science of thermometry, as ordinarily studied, is based upon the changes produced in bodies by heat. Among these we may mention change in volume, pressure, state of aggregation, dissociation, amount and color of light reflected, transmitted, or emitted, hardness, pyro-electric and thermo-electric properties, electric conductivity or specific induction capacity, magnetic properties, thermo-dynamic properties, &c.; and on each of these may be based a system of thermometry, each one of which is perfect in itself, but which differs from all the others widely. Indeed, each method may be applied to nearly all the bodies in nature, and hundreds or thousands of thermometric scales may be produced, which may be made to agree at two fixed points, such as the freezing and boiling points of water, but which will in general differ at nearly, if not all, other points.

But from the way in which the science has advanced, it has come to pass that all methods of thermometry in general use to the present time have been reduced to two or three, based respectively on the apparent expansion of mercury in glass and on the absolute expansion of some gas, and more lately on the second law of thermodynamics.

Each of these systems is perfectly correct in itself, and we have no right to designate either of them as incorrect. We must decide *a priori* on some system, and then express all our results in that system: the accuracy of science demands that there should be no

ambiguity on that subject. In deciding among the three systems, we should be guided by the following rules:—

1st. The system should be perfectly definite, so that the same temperature should be indicated, whatever the thermometer.

2d. The system should lead to the most simple laws in nature.

Sir William Thomson's absolute system of thermometry, coinciding with that based on the expansion of a perfect gas, satisfies these most nearly. The mercurial thermometer is not definite unless the kind of glass is given, and even then it may vary according to the way the bulb is blown. The gas thermometer, unless the kind of gas is given, is not definite. And, further, if the temperature as given by either of these thermometers was introduced into the equations of thermodynamics, the simplest of them would immediately become complicated.

Throughout a small range of temperature, these systems agree more or less completely, and it is the habit even with many eminent physicists to regard them as coincident between the freezing and boiling points of water. We shall see, however, that the difference between them is of the highest importance in thermometry, especially where differences of temperature are to be used.

For these reasons I have reduced all my measures to the absolute system.

The relation between the absolute system and the system based on the expansion of gases has been determined by Joule and Thomson in their experiments on the flow of gases through porous plugs (*Philosophical Transactions* for 1862, p. 579). Air was one of the most important substances they experimented upon.

To measure temperature on the absolute scale, we have thus only to determine the temperature on the air thermometer, and then reduce to the absolute scale. But as the air thermometer is very inconvenient to use, it is generally more convenient to use a mercurial thermometer which has been compared with the air thermometer. Also, for small changes of temperature the air thermometer is not sufficiently sensitive, and a mercurial thermometer is necessary for interpolation. I shall occupy myself first with a careful study of the mercurial thermometer.

#### (b.) The Mercurial Thermometer.

Of the two kinds of mercurial thermometers, the weight thermometer is of little importance to our subject. I shall therefore confine myself principally to that form having a graduated stem. For

convenience in use and in calibration, the principal bulb should be elongated, and another small bulb should be blown at the top. This latter is also of the utmost importance to the accuracy of the instrument, and is placed there by nearly all makers of standards.\* It is used to place some of the mercury in while calibrating, as well as when a high temperature is to be measured; also, the mercury in the larger bulb can be made free from air-bubbles by its means.

Most standard thermometers are graduated to degrees; but Regnault preferred to have his thermometers graduated to parts of equal capacity whose value was arbitrary, and others have used a single millimeter division. As thermometers change with age, the last two methods are the best; and of the two I prefer the latter where the highest accuracy is desired, seeing that it leaves less to the maker and more to the scientist. The cross-section of the tube changes continuously from point to point, and therefore the distribution of marks on the tube should be continuous, which would involve a change of the dividing engine for each division. But as the maker divides his tube, he only changes the length of his divisions every now and then, so as to average his errors. This gives a sufficiently exact graduation for large ranges of temperature; but for small, great errors may be introduced. Where there is an arbitrary scale of millimeters, I believe it is possible to calibrate the tube so that the errors shall be less than can be seen with the naked eye, and that the table found shall represent very exactly the gradual variation of the tube.

In the calibration of my thermometers with the millimetric scale, I have used several methods, all of which are based upon some graphical method. The first, which gives all the irregularities of the tube with great exactness, is as follows.

A portion of the mercury having been put in the upper bulb, so as to leave the tube free, a column about 15<sup>mm</sup>. long is separated off. This is moved from point to point of the tube, and its length carefully measured on the dividing engine. It is not generally necessary to move the column its own length every time, but it may be moved 20<sup>mm</sup>. or 25<sup>mm</sup>., a record of the position of its centre being kept. To eliminate any errors of division or of the dividing engine, readings were then taken on the scale, and the lengths reduced to their value in scale divisions. The area of the tube at every point is inversely as the length of the column. We shall thus have a series of figures nearly equal to each other, if the tube is good. By subtracting the

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\* Geissler and Casella omit it, which should condemn their thermometers.

smallest from each of the others, and plotting the results as ordinates, with the thermometer scale as abscissas, and drawing a curve through the points so found, we have means of finding the area at any point. The curve should not be drawn exactly through the points, but rather around them, seeing they are the average areas for some distance each side of the point. With good judgment, the curve can be drawn with great accuracy. I then draw ordinates every 10<sup>mm</sup>, and estimate the average area of the tube for that distance, which I set down in a table. As the lengths are uniform, the volume of the tube to any point is found by adding up the areas to that point.

But it would be unwise to trust such a method for very long tubes, seeing the mercury column is so short, and the columns are not end to end. Hence I use it only as supplementary to one where the column is about 50<sup>mm</sup> long, and is always moved its own length. This establishes the volumes to a series of points about 50<sup>mm</sup> apart, and the other table is only used to interpolate in this one. There seems to be no practical object in using columns longer than this.

Having finally constructed the arbitrary table of volumes, I then test it by reading with the eye the length of a long mercury column. No certain error was thus found at any point of any of the thermometers which I have used in these experiments.

While measuring the column, great care must be taken to preserve all parts of the tube at a uniform temperature, and only the extreme ends must be touched with the hands, which should be covered with cloth.

If  $V$  is the volume on this arbitrary scale, the temperature on the mercurial thermometer is found from the formula  $T = C V - t_0$ , where  $C$  and  $t_0$  are constants to be determined. If the thermometer contains the 0° and 100° points, we have simply

$$C = \frac{100}{V_{100} - V_0}.$$

Otherwise  $C$  is found by comparison with some other thermometer, which must be of the same kind of glass.

It is to be carefully noted that the temperature on the mercurial thermometer, as I have defined it, is proportional to the apparent expansion of mercury as measured on the stem. By defining it as proportional to the true volume of mercury in the stem, we have to introduce a correction to ordinary thermometers, as Poggendorf has shown. As I only use the mercurial thermometer to compare with the air thermometer, and as either definition is equally correct, I will

not further discuss the matter, but will use the first definition, as being the simplest.

In the above formula I have implicitly assumed that the apparent expansion is only a function of the temperature; but in solid bodies like glass there seems to be a progressive change in the volume as time advances, and especially after it has been heated. And hence in mercurial and alcohol thermometers, and probably in general in all thermometers which depend more or less on the expansion of solid bodies, we find that the reading of the thermometer depends, not only on its present temperature, but also on that to which it has been subjected within a short time; so that, on heating a thermometer up to a certain temperature, it does not stand at the same point as if it had been cooled from a higher temperature to the given temperature. As these effects are without doubt due to the glass envelope, we might greatly diminish them by using thermometers filled with liquids which expand more than mercury: there are many of these which expand six or eight times as much, and so the irregularity might be diminished in this ratio. But in this case we should find that the correction for that part of the stem which was outside the vessel whose temperature we were determining would be increased in the same proportion; and besides, as all the liquids are quite volatile, or at least wet the glass, there would be an irregularity introduced on that account. A thermometer with liquid in the bulb and mercury in the stem would obviate these inconveniences; but even in this case the stem would have to be calibrated before the thermometer was made. By a comparison with the air-thermometer, a proper formula could be obtained for finding the temperature.

But I hardly believe that any thermometer superior to the mercurial can at present be made,—that is, any thermometer within the same compass as a mercurial thermometer,—and I think that the best result for small ranges of temperature can be obtained with it by studying and avoiding all its sources of error.

To judge somewhat of the laws of the change of zero within the limits of temperature which I wished to use, I took thermometer No. 6163, which had lain in its case during four months at an average temperature of about  $20^{\circ}$  or  $25^{\circ}$  C., and observed the zero point, after heating to various temperatures, with the following result. The time of heating was only a few minutes, and the zero point was taken immediately after; some fifteen minutes, however, being necessary for the thermometer to entirely cool.

TABLE I.—SHOWING CHANGE OF ZERO POINT.

Temperature of Bulb before finding the 0 Point.	Change of 0 Point.	Temperature of Bulb before finding the 0 Point.	Change of 0 Point.
22.5	0	70.0	—0.115
30.0	—0.016	81.0	—0.170
40.5	—0.033	90.0	—0.231
51.0	—0.039	100.0	—0.318
60.0	—0.105	100.0	—0.347

The second 100° reading was taken after boiling for some time.

It is seen that the zero point is always lower after heating, and that in the limits of the table the lowering of the zero is about proportional to the square of the increase of temperature above 25° C. This law is not true much above 100°, and above a certain temperature the phenomenon is reversed, and the zero point is higher after heating; but for the given range it seems quite exact.

It is not my purpose to make a complete study of this phenomenon with a view to correcting the thermometer, although this has been undertaken by others. But we see from the table that the error cannot exceed certain limits. The range of temperature which I have used in each experiment is from 20° to 30° C., and the temperature rarely rose above 40° C. The change of zero in this range only amounts to 0°.03 C.

The exact distribution of the error from this cause throughout the scale has never been determined, and it affects my results so little that I have not considered it worth investigating. It seems probable, however, that the error is distributed throughout the scale. If it were uniformly distributed, the value of each division would be less than before by the ratio of the lowering at zero to the temperature to which the thermometer was heated.

The maximum errors produced in my thermometers by this cause would thus amount to 1 in 1300 nearly for the 40° thermometer, and to about 1 in 2000 for the others. Rather than allow for this, it is better to allow time for the thermometer to resume its original state.

Only a few observations were made upon the rapidity with which the zero returned to its original position. After heating to 81°, the zero returned from —0°.170 to —0°.148 in two hours and a half. After heating to 100°, the zero returned from —0°.347 to —0°.110 in nine days, and to —0°.022 in one month. Reasoning from this, I

should say that in one week thermometers which had not been heated above  $40^{\circ}$  should be ready for use again, the error being then supposed to be less than 1 in 4000, and this would be partially eliminated by comparing with the air thermometer at the same intervals as the thermometer is used, or at least heating to  $40^{\circ}$  one week before comparing with the air thermometer.

As stated before, when a thermometer is heated to a very high point, its zero point is raised instead of lowered, and it seems probable that at some higher point the direction of change is reversed again; for, after the instrument comes from the maker, the zero point constantly rises until it may be  $0^{\circ}.6$  above the mark on the tube. This gradual change is of no importance in my experiments, as I only use differences of temperature, and also as it was almost inappreciable in my thermometers.

Another source of error in thermometers is that due to the pressure on the bulb. In determining the freezing point, large errors may be made, amounting to several hundredths of a degree, by the pressure of pieces of ice. In my experiments, the zero point was determined in ice, and then the thermometer was immersed in the water of the comparator at a depth of about  $60^{\text{cm}}$ . The pressure of this water affected the thermometer to the extent of about  $0^{\circ}.01$ , and a correction was accordingly made. As differences of temperature were only needed, no correction was made for variation in pressure of the air.

It does not seem to me well to use thermometers with too small a stem, as I have no doubt that they are subject to much greater irregularities than those with a coarse bore. For the capillary action always exerts a pressure on the bulb. Hence, when the mercury rises, the pressure is due to a *rising* meniscus which causes greater pressure than the *falling* meniscus. Hence, an *apparent friction* of the mercurial column. Also, the capillary constant of mercury seems to depend on the electric potential of its surface, which may not be constant, and would thus cause an irregularity.

My own thermometers did not show any apparent action of this kind, but Pfaundler and Plattner mention such an action, though they give another reason for it.

#### (c.) Relation of the Mercurial and Air Thermometers.

##### 1. GENERAL AND HISTORICAL REMARKS.

Since the time of Dulong and Petit, many experiments have been made on the difference between the mercurial and the air thermometer,

but unfortunately most of them have been at high temperatures. As weight thermometers have been used by some of the best experimenters, I shall commence by proving that the weight thermometer and stem thermometer give the same temperature; at the same time, however, obtaining a convenient formula for the comparison of the air thermometer with the mercurial.

For the expansion of mercury and of glass the following formulæ must hold:—

$$\text{For mercury, } V = V_0 (1 + \alpha t + \beta t^2 + \&c.);$$

$$\text{" glass, } V' = V'_0 (1 + \alpha t + \beta t^2 + \&c.).$$

In both the weight and stem thermometers we must have  $V = V'$ .

$$\therefore V'_0 = V_0 \frac{1 + \alpha t + \beta t^2 + \&c.}{1 + \alpha t + \beta t^2 + \&c.} = V_0 (1 + A t + B t^2 + \&c.),$$

where  $V'_0$  and  $V_0$  are the volumes of the glass and of the mercury reduced to zero, and  $t$  is the temperature on the air thermometer. The temperature by the weight thermometer is

$$T = 100 \frac{P_0 - P_t}{P_0 - P_{100}} \frac{P_{100}}{P_t} = 100 \frac{\frac{P_0}{P_t} - 1}{\frac{P_0}{P_{100}} - 1},$$

where  $P_0$ ,  $P_t$ , &c. are the weights of mercury in the bulb at  $0^\circ$  C.,  $t^\circ$  C., &c.

Now these weights are directly as the volumes of the mercury at  $0^\circ$ .

$$\therefore \frac{P_0}{P_t} = 1 + A t + B t^2 + \&c.,$$

seeing that  $V$  is constant.

$$\therefore T = 100 \frac{A t + B t^2 + \&c.}{100 A + (100)^2 B + \&c.}.$$

In the stem thermometers we have  $V_0$ , the volume of mercury at  $0^\circ$ , constant, and the volume of the glass that the mercury fills, reduced to  $0^\circ$ , variable. As the volume of the glass  $V'_0$  is the volume reduced to  $0^\circ$ , it will be proportional to the volume of bulb plus the volume of the tube *as read off on the scale* which should be on the tube.

$$\therefore T = 100 \frac{(V'_0)_t - (V'_0)_0}{(V'_0)_{100} - (V'_0)_0} = 100 \frac{\frac{(V'_0)_t}{(V'_0)_0} - 1}{\frac{(V'_0)_{100}}{(V'_0)_0} - 1};$$



$$\therefore T = 100 \frac{At + Bt^2 + \&c.}{100A + (100)^2 B^2 + \&c.},$$

which is the same as for the weight thermometer.

If the fixed points are  $0^\circ$  and  $t^\circ$  instead of  $0^\circ$  and  $100^\circ$ , we can write

$$T = t' \frac{At + Bt^2 + Ct^3 + \&c.}{At' + Bt'^2 + Ct'^3 + \&c.}$$

$$T = t \left\{ 1 + (t - t') \left\{ \frac{B}{A} + \frac{C}{A} + \frac{B^2}{A^2} t' + \frac{C}{A} t \right\} + \&c. \right\}$$

$$T = t \left\{ 1 + (t - t') \left[ \frac{B}{A} + \frac{B^2}{A^2} t' + \frac{C}{A} (t + t') \right] + \&c. \right\}$$

As  $T$  and  $t$  are nearly equal, and as we shall determine the constants experimentally, we may write

$$t = T - a t (t' - t) (b - t) + \&c.,$$

where  $t$  is the temperature on the air thermometer, and  $T$  that on the mercurial thermometer, and  $a$  and  $b$  are constants to be determined for each thermometer.

The formula might be expanded still further, but I think there are few cases which it will not represent as it is. Considering  $b$  as equal to 0, a formula is obtained which has been used by others, and from which some very wrong conclusions have been drawn. In some kinds of glass there are three points which coincide with the air thermometer, and it requires at least an equation of the third degree to represent this.

The three points in which the two thermometers coincide are given by the roots of the equation

$$t (t' - t) (b - t) = 0,$$

and are, therefore,

$$t = 0$$

$$t = t'$$

$$t = b.$$

In the following discussion of the historical results, I shall take  $0^\circ$  and  $100^\circ$  as the fixed points. Hence,  $t' = 100^\circ$ . To obtain  $a$  and  $b$ , two observations are needed at some points at a distance from  $0^\circ$  and  $100^\circ$ . That we may get some idea of the values of the constants in the formula for different kinds of glass, I will discuss some of the experimental results of Regnault and others with this in view.

Regnault's results are embodied, for the most part, in tables given on p. 239 of the first volume of his *Relation des Expériences*. The figures given there are obtained from curves drawn to represent the mean of his experiments, and do not contain any theoretical results. The direct application of my formula to his experiments could hardly be made without immense labor in finding the most probable value of the constants.

But the following seem to satisfy the experiments quite well :—

Cristal de Choisy-le-Roi	$b = 0$ ,	$a = .000\ 000\ 32$ .
Verre Ordinaire	$b = 245^\circ$ ,	$a = .000\ 000\ 34$ .
Verre Vert	$b = 270^\circ$ ,	$a = .000\ 000\ 095$ .
Verre de Suède	$b = +10^\circ$ ,	$a = .000\ 000\ 14$ .

From these values I have calculated the following :—

TABLE II.—REGNAULT'S RESULTS COMPARED WITH THE FORMULA.

Air Thermom.	Choisy-le-Roi.			Verre Ordinaire.			Verre Vert.			Verre de Suède.		
	Observed.	Calculated.	Difference.	Observed.	Calculated.	Difference.	Observed.	Calculated.	Difference.	Observed.	Calculated.	Difference.
100	0	0	0	0	0	0	0	0	0	0	0	0
120	120.12	120.09	+ .03	119.93	119.90	+ .05	120.07	120.06	+ .01	120.04	120.04	0
140	140.20	140.25	— .04	139.96	139.80	+ .05	140.21	140.22	— .01	140.11	140.10	+ .01
160	160.32	160.49	— .03	159.74	159.72	+ .02	160.40	160.39	+ .01	160.20	160.21	— .01
180	180.80	180.83	— .03	179.63	179.68	— .05	180.60	180.62	— .02	180.33	180.34	— .01
200	201.25	201.28	— .03	199.70	199.69	+ .01	200.80	200.79	— .09	201.50	200.63	— .03
220	221.82	221.86	— .04	219.80	219.78	+ .02	221.20	221.23	— .03	220.75	220.78	— .03
240	242.55	242.56	— .01	239.90	239.96	— .06	241.00	241.03	— .03	241.16	241.08	+ .08
260	263.44	263.46	— .02	260.20	260.21	— .01	262.15	262.09	+ .07			
280	284.48	284.52	— .04	280.58	280.00	— .02	282.85	282.63	+ .22			
300	305.72	305.76	— .04	301.08	301.12	— .04						
320	327.25	327.20	— .05	321.80	321.80	00						
340	349.30	348.88	+ .42	344.00	342.64	+ .36						

The formula, as we see from the table, represents all Regnault's curves with great accuracy, and if we turn to his experimental results we shall find that the deviation is far within the limits of the experimental errors. The greatest deviation happens at  $340^\circ$ , and may be accounted for by an error in drawing the curve, as there are few experimental results so high as this, and the formula seems to agree with them almost as well as Regnault's own curve.

The object of comparing the formula with Regnault's results at temperatures so much higher than I need, is simply to test the formula through as great a range of temperatures, and for as many kinds of

\* Corrected from 280.52 in Regnault's table.

glass, as possible. If it agrees reasonably well throughout a great range, it will probably be very accurate for a small range, provided we obtain the constants to represent that small range the best.

Having obtained a formula to represent any series of experiments, we can hardly expect it to hold for points outside our series, or even for interpolating between experiments too far apart, as, very often, a small change in one of the constants may affect the part we have not experimented on in a very marked manner. Thus in applying the formula to points between  $0^\circ$  and  $100^\circ$  the value of  $b$  will affect the result very much. In the case of the glass Choisy-le-Roi many values of  $b$  will satisfy the observations besides  $b = 0$ . For the ordinary glass, however,  $b$  is well determined, and the formula is of more value between  $0^\circ$  and  $100^\circ$ .

The following table gives the results of the calculation.

TABLE III. — REGNAULT'S RESULTS COMPARED WITH THE FORMULA.

Air Thermome- ter.	Calculated $\alpha = .000\ 000\ 82$ $b = 0$ .	Calculated $\alpha = .000\ 000\ 84$ $b = 246$ .	Observed.	$\Delta$	Calculated $\alpha = .000\ 000\ 44$ $b = 260$ .	$\Delta$
	Choisy-le-Roi.	Verre Ordinaire.	Verre Ordinaire.		Verre Ordinaire.	
0	0	0	0	....	0	....
10	10.00	10.07	....	....	10.10	....
20	19.99	20.12	....	....	20.17	....
30	29.98	30.15	30.12	+.08	30.21	+.09
40	39.97	40.17	40.23	-.06	40.23	0
50	49.96	50.17	50.23	-.06	50.23	0
60	59.95	60.15	60.24	-.09	60.21	-.03
70	69.95	70.12	70.22	-.10	70.18	-.04
80	79.96	80.09	80.10	-.01	80.11	+.01
90	89.97	90.05	....	....	90.07	....
100	100	100	100	....	100	....

Regnault does not seem to have published any experiments on Choisy-le-Roi glass between  $0^\circ$  and  $100^\circ$ , but in the table between pp. 226, 227, there are some results for ordinary glass. The separate observations do not seem to have been very good, but by combining the total number of observations I have found the results given above. The numbers in the fourth column are found by taking the mean of Regnault's results for points as near the given temperature as possible. The agreement is only fair, but we must remember that the same specimens of glass were not used in this experiment as in the others, and that for these specimens the agreement is also poor above  $100^\circ$ . The values  $\alpha = .000\ 000\ 44$  and  $b = 260^\circ$  are much better

for these specimens, and the seventh column contains the values calculated from these values. These values also satisfy the observations above 100° for the given specimens.

The table seems to show that between 0° and 100° a thermometer of Choisy-le-Roi almost exactly agrees with the air thermometer. But this is not at all conclusive. Regnault, however, remarks,\* that between 0° and 100° thermometers of this glass agree more nearly with the air thermometer than those of ordinary glass, though he states the difference to amount to .1 to .2 of a degree, the mercurial thermometer standing *below* the air thermometer. With the exception of this remark of Regnault's, no experiments have ever been published in which the direction of the deviation was similar to this. All experimenters have found the mercurial thermometer to stand *above* the air thermometer between 0° and 100°, and my own experiments agree with this. However, no general rule for all kinds of glass can be laid down.

Boscha has given an excellent study of Regnault's results on this subject, though I cannot agree with all his conclusions on this subject. In discussing the difference between 0 and 100° he uses a formula of the form

$$T - t = \frac{b}{a} t (100 - t),$$

and deduces from it the erroneous conclusion that the difference is greatest at 50° C., instead of between 40° and 50°. His results for  $T - t$  at 50° are

Choisy-le-Roi . . . . .	— .22
Verre Ordinaire . . . . .	+ .25
Verre Vert . . . . .	+ .14
Verre de Suède . . . . .	+ .56

and these are probably somewhat nearly correct, except the negative value for Choisy-le-Roi.

With the exception of Regnault, very few observers have taken up this subject. Among these, however, we may mention Recknagel, who has made the determination for common glass between 0° and 100°. I have found approximately the constants for my formula in this case, and have calculated the values in the fourth column of the following table.

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\* Comptes Rendus, lxi.

TABLE IV.—RECKNAGEL'S RESULTS COMPARED WITH THE FORMULA.

Air Thermometer.	Mercurial Thermometer.		Difference.
	Observed.	Calculated.	
0	0	0	0
10	10.08	10.08	0
20	20.14	20.14	0
30	30.18	30.18	0
40	40.20	40.20	0
50	50.20	50.20	0
60	60.18	60.18	0
70	70.14	70.15	+.01
80	80.10	80.11	+.01
90	90.05	90.06	+.01
100	100.00	0	0

$$b = 290^\circ \quad a = .000\ 000\ 33$$

$$T = t + a\ t(100 - t)(b - t)$$

It will be seen that the values of the constants are not very different from those which satisfy Regnault's experiments.

There seems to be no doubt, from all the experiments we have now discussed, that the point of maximum difference is not at  $50^\circ$ , but at some less temperature, as  $40^\circ$  to  $45^\circ$ , and this agrees with my own experiments, and a recent statement by Ellis in the *Philosophical Magazine*. And I think the discussion has proved beyond doubt that the formula is sufficiently accurate to express the difference of the mercurial and air thermometers throughout at least a range of  $200^\circ$ , and hence is probably very accurate for the range of only  $100^\circ$  between  $0^\circ$  and  $100^\circ$ .

Hence it is only necessary to find the constants for my thermometers. But before doing this it will be well to see how exact the comparison must be. As the thermometers are to be used in a calorimetric research in which differences of temperature enter, the error of the mercurial compared with the air thermometer will be

$$\frac{dT}{dt} - 1 = a \{ b t - 2(b + t)t + 3t^2 \},$$

which for the constants used in Recknagel's table becomes

$$\text{Error} = \frac{dT}{dt} - 1 = .000\ 000\ 33 \{ 29000. - 780t + 3t^2 \}.$$

This amounts to nearly one per cent at  $0^\circ$ , and thence decreases to  $45^\circ$ , after which it increases again. As only  $0.2$  at the  $40^\circ$  point

produces this large error at  $0^\circ$ , it follows that an error of only  $0^\circ.02$  at  $40^\circ$  will produce an error of  $\frac{1}{1000}$  at  $0^\circ$ . At other points the errors will be less.

Hence extreme care must be taken in the comparison and the most accurate apparatus must be constructed for the purpose.

## 2. DESCRIPTION OF APPARATUS.

### *The Air Thermometer.*

In designing the apparatus, I have have had in view the production of a uniform temperature combined with ease of reading the thermometers, which must be totally immersed in the water. The uniformity, however, needed only to apply to the air thermometer and to the bulbs of the mercurial thermometer, as a slight variation in the temperature of the stems is of no consequence. A uniform temperature for the air thermometer is important, because it must take time for a mass of air to heat up to a given temperature within  $0^\circ.01$  or less.

Fig. 1 gives a section of the apparatus. This consists of a large copper vessel, nickel-plated on the outside, with double walls an inch apart, and made in two parts, so that it could be put together water-tight along the line  $ab$ . As seen from the dimensions, it required about 28 kilogrammes of water to fill it. Inside of this was the vessel  $mdefghkl n$ , which could be separated along the line  $dk$ . In the upper part of this vessel, a piston,  $q$ , worked, and could draw the water from the vessel. The top was closed by a loose piece of metal,  $op$ , which fell down and acted as a valve. The bottom of this inner vessel had a false bottom,  $cl$ , above which was a row of large holes; above these was a perforated diaphragm,  $s$ . The bulb of the air thermometer was at  $t$ , with the bulbs of the mercurial thermometers almost touching it. The air thermometer bulb was very much elongated, being about 18<sup>cm.</sup> long and 3 to 5<sup>cm.</sup> in diameter. Although the bulbs of the thermometers were in the inner vessel, the stems were in the outer one, and the reading was accomplished through the thick glass window  $uv$ .

The change of the temperature was effected by means of a Bunsen burner under the vessel  $w$ .

The working of the apparatus was as follows. The temperature having been raised to the required point, the piston  $q$  was worked to stir up the water; this it did by drawing the water through the holes at  $cl$  and the perforated diaphragm  $s$ , and thence up through the

apparatus to return on the outside. When the whole of the water is at a nearly uniform temperature the stirring is stopped, the valve *op* falls into place, and the connection of the water in the outer and inner vessels is practically closed as far as currents are concerned, and

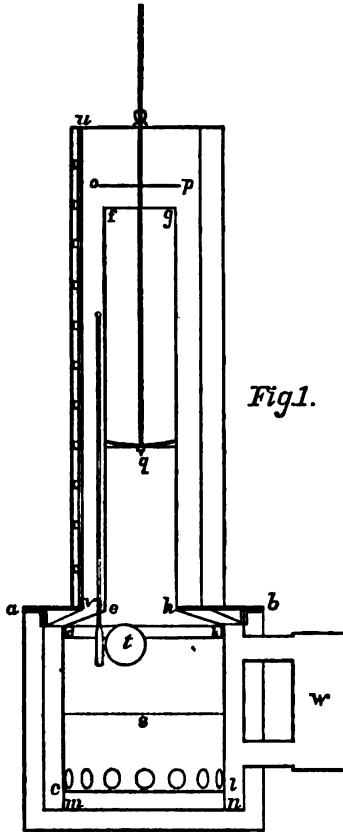


Fig. 1.

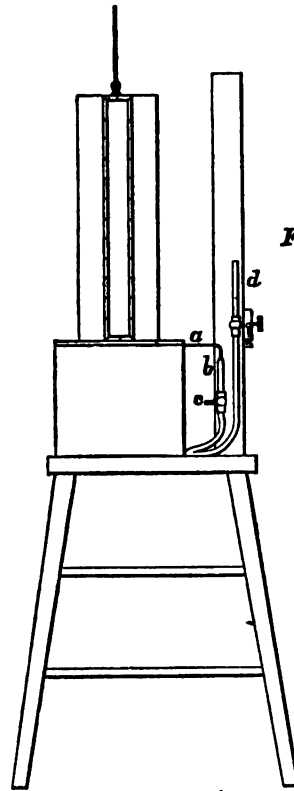


Fig. 2.

before the water inside can cool a little the outer water must have cooled considerably.

So effective was this arrangement that, although some of the thermometers read to  $0^{\circ}.007$  C., yet they would remain perfectly stationary for several minutes, even when at  $40^{\circ}$  C. At very high temperatures, such as  $80^{\circ}$  or  $90^{\circ}$  C., the burner was kept under the vessel *w* all the time, and supplied the loss of the outer vessel by radiation. The inner vessel would under these circumstances remain at a very

constant temperature. The water in the outer vessel never differed by more than a small fraction of a degree from that in the inner one.

To get the 0 and 100° points the upper parts of the vessel above the line *a b* were removed, and ice placed around the bulb of the air thermometer, and left for several hours, until no further lowering took place. For the 100° point the copper vessel shown in Fig. 3 was used. The portion *y* of this vessel fitted directly over the bulb of the air thermometer. On boiling water in *x*, the steam passed through the tube to the air thermometer. It is with considerable difficulty that the 100° point is accurately reached, and, unless care be taken, the bulb will be at a slightly lower temperature. Not only must the bulb be in the steam, but the walls of the cavity must also be at 100°. To accomplish this in this case, a large mass of cloth was heaped over the instrument, and then the water in *x* vigorously boiled for an hour or so. After fifteen minutes there was generally no perceptible increase of temperature, though an hour was allowed so as to make certain.

The external appearance of the apparatus is seen in Fig. 2. The method of measuring the pressure was in some respects similar to that used in the air thermometer of Jolly, except that the reading was taken by a cathetometer rather than by a scale on a mirror. The capillary stem of the air thermometer leaves the water vessel at *a*, and passes to the tube *b*, which is joined to the three-way cock *c*. The lower part of the cock is joined by a rubber tube to another glass tube at *d*, which can be raised and lowered to any extent, and has also a fine adjustment. These tubes were about 1.5<sup>cm</sup> diameter on the inside, so that there should be little or no error from capillarity. Both tubes were exactly of the same size, and for a similar reason.

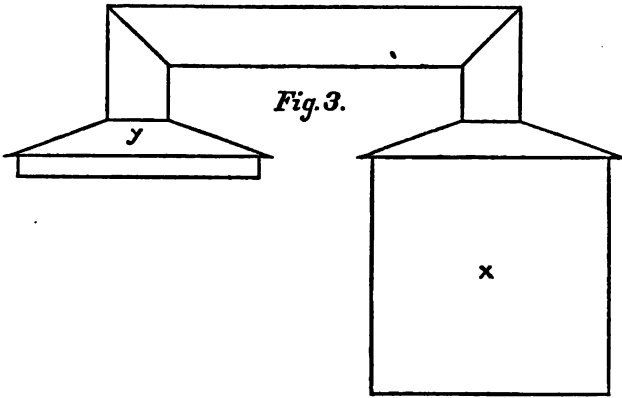
The three-way cock is used to fill the apparatus with dry air, and also to determine the capacity of the tube above a given mark. In filling the bulb, the air was pumped out about twenty times, and allowed to enter through tubes containing chloride of calcium, sulphuric acid, and caustic soda, so as to absorb the water and the carbonic acid.

#### *The Cathetometer.*

The cathetometer was one made by Meyerstein, and was selected because of the form of slide used. The support was round, and the telescope was attached to a sleeve which exactly fitted the support. The greatest error of cathetometers arises from the upright support not being exactly true, so that the telescope will not remain in level



at all heights. It is true that the level should be constantly adjusted, but it is also true that an instrument can be made where such an adjustment is not necessary. And where time is an element in the accuracy, such an instrument should be used. In the present case it was absolutely necessary to read as quickly as possible, so as not to leave time for the column to change. In the first place the round column, when made, was turned in a lathe to nearly its final dimensions. The line joining the centres of the sections must then have been very accurately straight. In the subsequent fitting some slight irregularities must have been introduced, but they could not have been great with good workmanship.\* The upright column was fixed, and the telescope moved around it by a sleeve on the other sleeve. Where



the objects to be measured are not situated at a very wide angle from each other, this is a good arrangement, and has the advantage that any side of the column can be turned toward the object, and so, even if it were crooked, we could yet turn it into such a position as to nearly eliminate error.

It was used at a distance of about 110<sup>mm</sup> from the object, and no difficulty was found after practice in setting it on the column to  $\frac{1}{10}$ <sup>mm</sup> at least. The cross hairs made an angle of 45° with the horizontal, as this was found to be the most sensitive arrangement.

The scale was carefully calibrated, and the relative errors† for the

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\* The change of level along the portion generally used did not amount to more than .1 of a division, or about .01<sup>mm</sup> at the mercury column, as this is about the smallest quantity which could be observed on the level.

† These amounted to less than .016<sup>mm</sup> at any part.

portion used were determined for every centimeter, the portion of the scale between the  $0^\circ$  and  $100^\circ$  points of the air thermometer being assumed correct. There is no object in determining the absolute value of the scale, but it should agree reasonably well with that on the barometer; for let  $H_0$ ,  $H_t$ , and  $H_{100}$  be the readings of the barometer, and  $h_0$ ,  $h_t$ , and  $h_{100}$  the readings of the cathetometer at the temperatures denoted by the suffix. Then approximately

$$t = \frac{(H_t + h_t) - (H_0 + h_0)}{(H_{100} + h_{100}) - (H_0 + h_0)} = \frac{H_t - H_0 + h_t - h_0}{H_{100} - H_0 + h_{100} - h_0}.$$

As the height of the barometer varies only very slightly during an experiment, the value of this expression is very nearly

$$\frac{h_t - h_0}{h_{100} - h_0},$$

which does not depend on the absolute value of the scale divisions.

But the best manner of testing a cathetometer is to take readings upon an accurate scale placed near the mercury columns to be measured. I tried this with my instrument, and found that it agreed with the scale to within two or three one-hundredths of a millimeter, which was as near as I could read on such an object.

In conclusion, every care was taken to eliminate the errors of this instrument, as the possibility of such errors was constantly present in my mind; and it is supposed that the instrumental errors did not amount to more than one or two one-hundredths of a millimeter on the mercury column. The proof of this will be shown in the results obtained.

#### *The Barometer.*

This was of the form designed by Fortin, and was made by James Green of New York. The tube was 2.0<sup>cm</sup> diameter nearly on the outside, and about 1.7<sup>cm</sup> on the inside. The correction for capillarity is therefore almost inappreciable, especially as, when it remains constant, it is exactly eliminated from the equation. The depression for this diameter is about .08<sup>mm</sup>, but depends upon the height of the meniscus. The height of the meniscus was generally about 1.3<sup>mm</sup>; but according as it was a rising or falling meniscus, it varied from 1.4 to 1.2<sup>mm</sup>. These are the practical values of the variation, and would have been greater if the barometer had not been attached to the wall a little loosely, so as to have a slight motion when handled. Also in use the instrument was slightly tapped before read-

ing. The variation of the height of the meniscus from 1.2 to 1.4<sup>mm</sup> would affect the reading only to the extent of .01 to .02<sup>mm</sup>.

The only case where any correction for capillarity is needed is in finding the temperatures of the steam at the 100° point, and will then affect that temperature only to the extent of about 0°.005.

The scale of the instrument was very nearly standard at 0° C., and was on brass.

At the centre of the brass tube which surrounded the barometer, a thermometer was fixed, the bulb being surrounded by brass, and therefore indicating the temperature of the brass tube.

In order that it should also indicate the temperature of the barometer, the whole tube and thermometer were wrapped in cloth until a thickness of about 5 or 6<sup>cm</sup> was laid over the tube, a portion being displaced to read the thermometers. This wrapping of the barometer was very important, and only poor results were obtained before its use; and this is seen from the fact that 1° on the thermometer indicates a correction of .12<sup>mm</sup> on the barometer, and hence makes a difference of 0°.04 on the air thermometer.

As this is one of the most important sources of error, I have now devised means of almost entirely eliminating it, and making continual reading of the barometer unnecessary. This I intend doing by an artificial atmosphere, consisting of a large vessel of air in ice, and attached to the open tube of the manometer of the air thermometer.

#### *The Thermometers.*

The standard thermometers used in my experiments are given in the following table.

TABLE V.—STANDARD THERMOMETERS.\*

Mark.	Approximate Length in Centimeters.	Range.	Graduation.	Length occupied by 1° C.	Maker.	When made.	Owner or Lender.
6167	65	0 to 100°	Millimeter.	...	Baudin	1876-7	Physical Laboratory, Johns Hopkins University.
6163	50	-6° to 40°	"	9.0	"	"	"
6165	50	-3° to 33°	"	11.7	"	"	"
6166	50	-2° to 31°	"	12.9	"	"	"
Kew 104	66	-21° to 108°	0°-5 F.	4.6	Welsh.	July, 1853	Prof. Barker, Univ. of Pennsylvania.
Geissler	45	-3° to 102°	0°-1 C.	3.8	Geissler.	(?)	Chemical Laboratory, Johns Hopkins University.
868	48	Nearly 0 to 100°	Arbitrary { equal volumes }	3.2	Fastré.	1851	Prof. Gibbs, Harvard Coll.
876	48	Nearly 0 to 100°	"	3.1	"	"	"
3235	{ About 40 }	{ 32° F. to 212° or more. }	1° F.	1.6	Casella.	(?)	Prof. Pickering, Harvard Observatory.
32378	46	-15° to 110°	0°-2 C.	3.2	"	{ See Kew Register for 1873, -4, -8. }	Prof. Trowbridge, Harvard College.
7316	61	-1° to +101°	0°-1 C.	4.9	Baudin.	Oct., 1878	Physical Laboratory, Johns Hopkins University.
7334	61	0° to 100°	0°-1 C.	4.9	"	"	{ S. W. Holman, Mass. Inst. of Technology. }

\* Besides these there were several other standards at my disposal. One from Salleron was not well calibrated, and several with millimeter scale, by Baudin, have not yet been calibrated. I have also several by Baudin graduated to 0°-2 C., which, although good, are not his best work. The comparison of the last six of which were brought here by Mr. Holman for comparison, is given in the Appendix to this part of my paper. I am much indebted to Prof. Barker for the use of his Kew standard, and to Mr. Holman for the use of his tables of comparison.

The calibration of the first four thermometers has been described. The calibration of the Kew standard was almost perfect, and no correction was thought necessary. The scale divided on the tube was to half-degrees Fahrenheit; but as the  $32^{\circ}$  and  $212^{\circ}$  points were not correct, it was in practice used as a thermometer with arbitrary divisions. The interval between the  $0^{\circ}$  and  $100^{\circ}$  points, as Welsh found it, was  $180^{\circ}.12$ , using barometer at 30 inches, or  $180^{\circ}.05$  as corrected to 760<sup>mm</sup> of mercury.\* At the present time it is  $179^{\circ}.68$ ,† showing a change of 1 part in 486 in twenty-five years. This fact shows that the ordinary method of correcting for change of zero is not correct, and that the coefficient of expansion of glass changes with time.‡

I have not been able to find any reference to the kind of glass used in this thermometer. But in a report by Mr. Welsh we find a comparison, made on March 19, 1852, of some of his thermometers with two other thermometers, — one by Fastré, examined and approved by Regnault, and the other by Troughton and Simms. The thermometer which I used was made a little more than a year after this; and it is reasonable to suppose that the glass was from the same source as the standards Nos. 4 and 14 there used. We also know that Regnault was consulted as to the methods, and that the apparatus for calibration was obtained under his direction.

I reproduce the table here with some alterations, the principal one of which is the correction of the Troughton and Simms thermometers, so as to read correctly at  $32^{\circ}$  and  $212^{\circ}$ , the calibration being assumed correct, but the divisions arbitrary.

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* Boiling point,	Welsh,	Aug. 17, 1853,	$212^{\circ}.17$ ; barometer 30 <sup>in</sup> .
Freezing point,	"	"	$32^{\circ}.05$ .
Boiling point,	Rowland,	June 22, 1878,	$212^{\circ}.46$ ; barometer 760 <sup>mm</sup> .
Freezing point,	"	"	$32^{\circ}.78$ .

The freezing point was taken before the boiling point in either case.

†  $179^{\circ}.70$ , as determined again in January, 1879.

‡ The increase shown here is 1 in 80 nearly! It is evidently connected with the change of zero; for when glass has been heated to  $100^{\circ}$ , the mean coefficient of expansion between 0 and  $100^{\circ}$  often changes as much as 1 in 50. Hence it is not strange that it should change 1 in 80 in twenty-five years. I believe this fact has been noticed in the case of standards of length.

TABLE VI. — COMPARISON BY WELSH, 1852.

Mean of Kew Standards Nos. 4 and 14.	Fastré 231, Regnault.	$\Delta$ Kew.	Troughton and Simms (Royal Society).	$\Delta$ Kew.
82.00	82.00	0	82.00	0
88.71	88.72	+ .01	88.70	— .01
45.04	45.03	— .01	45.03	— .01
49.96	49.96	.00	49.96	.00
55.34	55.37	+ .03	55.34	.00
60.07	60.06	— .02	60.06	— .01
65.39	65.41	+ .02	65.36	— .03
69.93	69.95	+ .02	69.93	.00
74.69	74.69	.00	74.72	+ .03
80.05	80.06	+ .01	80.14	+ .09
85.80	85.38	+ .03	85.44	+ .14
90.50	90.51	+ .01	90.56	+ .06
95.28	95.24	— .02	95.40	+ .14
101.77	101.77	.00	101.94	+ .15
109.16	109.15	— .01	109.25	+ .08
212.00	212.00	.00	212.00	.00

It is seen that the Kew standards and the Fastré agree perfectly, but that the Troughton and Simms standard stands above the Kew thermometers at 100° F.

The Geissler standard was made by Geissler of Bonn, and its scale was on a piece of milk glass, enclosed in a tube with the stem. The calibration was fair, the greatest error being about 0°.015 C., at 50° C.; but no correction for calibration was made, as the instrument was only used as a check for the other thermometers.

### 8. RESULTS OF COMPARISON.

#### *Calculation of Air Thermometer.*

This has already been described, and it only remains to discuss the formula and constants, and the accuracy with which the different quantities must be known.

The well-known formula for the air thermometer is

$$T = \frac{1}{a} \frac{H - h + \frac{v}{V} \left\{ H \frac{1+b't'}{1+at'} - h \frac{1+bt}{1+at} \right\} + bHT}{h - \frac{v}{V} \left\{ H \frac{1+b't'}{1+at'} - h \frac{1+bt}{1+at} \right\}}.$$

Solving with reference to  $T$ , and placing in a more convenient form, we have

$$T = \frac{1}{a} \frac{H - h' + \frac{v}{V} H \frac{1}{1+\gamma t}}{h' - \frac{v}{V} H \frac{1}{1+\gamma t} - H \frac{b}{a}} \text{ nearly,}$$

where

$$h' = h \left( 1 + \frac{v}{V} \frac{1}{1 + \gamma t} \right),$$

and

$$\gamma = \alpha - \beta = .00364.$$

For the first bulb,

$$\frac{v}{V} = .0057.$$

For the second bulb,

$$\frac{v}{V} = .0058.$$

To discuss the error of  $T$  due to errors in the constants, we must replace  $\alpha$  by its experimental value, seeing that it was determined with the same apparatus as that by which  $T$  was found. As it does not change very much, we may write approximately

$$T = 100 \frac{H - h}{H_{100} - h} \left\{ 1 - \frac{v}{V} \frac{1}{1 + \gamma t} \left( \frac{H_{100} - H}{h} \right) - \frac{\beta_{100} H_{100} - \beta H}{\alpha h} \right\}.$$

From this formula we can obtain by differentiation the error in each of the quantities, which would make an error of one tenth of one per cent in  $T$ . The values are for  $T = 40^\circ$  nearly;  $t = 20^\circ$ ;  $H_{100} - h = 270\text{mm}$ ; and  $h = 750\text{mm}$ . If  $x$  is the variable,

$$\Delta x = \frac{dx}{dT} \quad \Delta T = \frac{dx}{dT} \frac{T}{1000} = .04 \frac{dx}{dT}$$

TABLE VII — ERRORS PRODUCING AN ERROR IN  $T$  OF 1 IN 1000 AT  $40^\circ \text{C}$ .

	$H$	$H_{100}$ or $h$	$\frac{v}{V}$	$\frac{\beta_{100}}{\alpha}$ $\frac{\beta}{\alpha}$ constant.	$\frac{\beta_{100}}{\alpha}$ $\frac{\beta}{\alpha}$ constant.	$\frac{\beta_{100} - \beta}{\alpha}$ const.	$\frac{\beta_{100} - \beta}{\alpha}$ constant.
Absolute value, $\Delta x$	.11mm.	.27mm.	.005	.00074	.00087	.0047	.00087
Relative value, $\frac{\Delta x}{x}$	...	...	0.9	.10	.12	.62	...

From this table it would seem that there should be no difficulty in determining the  $40^\circ$  point on the air thermometer to at least 1 in 2000; and experience has justified this result. The principal difficulty is in the determination of  $H$ , seeing that this includes errors in reading the barometer as well as the cathetometer. For this reason, as mentioned before, I have designed another instrument for future use, in which the barometer is nearly dispensed with by use of an artificial atmosphere of constant pressure.

The value of  $\frac{v}{V}$  does not seem to affect the result to any great extent; and if it was omitted altogether, the error would be only

about 1 in 1,000, assuming that the temperature  $t$  was the same at the determination of the zero point, the 40° point, and the 100° point. It seldom varied much.

The coefficient of expansion of the glass influences the result very slightly, especially if we know the *difference* of the mean coefficients between 0° and 100°, and say  $-10^\circ$  and  $+10^\circ$ . This difference I at first determined from Regnault's tables, but afterwards made a determination of it, and have applied the correction.\*

The table given by Regnault is for one specimen of glass only; and I sought to better it by taking the expansion at 100° from the mean of the five specimens given by Regnault on p. 231 of the first volume of his *Relation des Expériences*, and reducing the numbers on page 237 in the same proportion. I thus found the values given in the second column of the following table.

TABLE VIII. — COEFFICIENT OF EXPANSION OF THE GLASS OF THE AIR THERMOMETER, ACCORDING TO THE AIR THERMOMETER.

Temperature according to Air Thermometer.	Values of $b$ used for a first Calculation	$b$ from Regnault's Table, Glass No. 5.	Experimental Results.			
			Apparent Coefficient of Expansion of Mercury.	$b$ , using Regnault's Value for Mercury.†	$b$ , using Recknagel's Value for Mercury.‡	$b$ , using Wüllner's Value for Mercury.§
0	.0000252	.0000268	.....	.....	.....	.....
20°	.0000253	.0000264	.00015410	.0000254	.0000264	.0000278
40°	.0000256	.0000267	.00015395	.0000258	.0000266	.0000276
60°	.0000259	.0000270	.00015391	.0000261	.0000267	.0000278
80°	.0000262	.0000273	.....	.....	.....	.....
100°	.0000264	.0000276	.00015381	.0000277	.0000277	.0000287

The second column contains the values which I have used, and one of the last three columns contains my experimental results, the last being probably the best. The errors by the use of the second column compared with the last are as follows:—

$$\frac{100}{100} \text{ from using } b_{100} - b_{40} = .0000008 \text{ instead of } .0000011;$$

$$\frac{70}{100} \text{ from using } b_{100} = .0000264 \text{ instead of } .0000287;$$

or,  $\frac{40}{100}$  for both together.

\* This was determined by means of a large weight thermometer in which the mercury had been carefully boiled. The glass was from the same tube as that of the air thermometer, and they were cut from it within a few inches of each other.

† *Relation des Expériences*, i. 328.

‡ *Pogg. Ann.*, cxxiii. 135.

§ *Experimental Physik*, Wüllner, i. 67.



As the error is so small, I have not thought it worth while to entirely recalculate the tables, but have calculated a table of corrections as follows, and have so corrected them:—

TABLE IX. — TABLE OF CORRECTIONS.

$T'$	$T$	Correction.
Calculated Temperature.	Corrected Temperature.	
0	0	0
10	9.9971	— .0029
20	19.9946	— .0054
30	29.9924	— .0076
40	39.9907	— .0098
50	49.9894	— .0106
60	59.9865	— .0185
80	79.9880	— .0120
100	100.	0

$$T = T' \{1 + 373 (b'_{100} - b_{100}) - (273 + T') (b' - b)\}.$$

$$T = T' \{1 - .000858 + (273 + T') (b - b')\}.$$

$T = .99975 T'$  approximately between 0 and 40°. This last is true within less than  $\frac{1}{1000}$  of a degree.

The two bulbs of the air thermometer used were from the same piece of glass tubing, and consequently had nearly, if not quite, the same coefficient of expansion.

In the reduction of the barometer and other mercurial columns to zero, the coefficient .000162 was used, seeing that all the scales were of brass.

In the tables the readings of the thermometers are reduced to volumes of the tube from the tables of calibration, and they are corrected for the pressure of water, which increased their reading, except at 0°, by about 0°.01 C.

The order of the readings was as follows in each observation:— 1st, barometer; 2d, cathetometer; 3d, thermometers forward and backward; 4th, cathetometer; 5th, barometer, &c., — repeating the same once or twice at each temperature. In the later observations, two series like the above were taken, and the water stirred between them.

The following results were obtained at various times for the value of  $\alpha$  with the first bulb:—

.0036664

.0036670

.0036658

.0036664

.0036676

Mean  $\alpha$  = .0036664

obtained by using the coefficient of expansion of glass .0000264 at 100°, or  $\alpha$  = .0036698, using the coefficient .0000287.

The thermometers Nos. 6163, 6165, 6166, were always taken out of the bath when the temperature of 40° was reached, except on November 14, when they remained in throughout the whole experiment.

The thermometer readings are reduced to volumes by the tables of calibration.

TABLE X. — 1ST SERIES, Nov. 14, 1877.

Relative Weight.	Air Thermometer.	V 6163.	V 6165.	V 6167.	Temperature by 6167.	$\Delta$
4	0	115.33	21.25	6.147	0	0
4	17°.1425	422.84	255.80	15.685	17°.661	.236
4	23°.793	534.71	341.05	19.157	24°.089	.296
5	30°.582	653.49	431.71	22.838	30°.896	.314
2	38°.569	798.18	...	27.175	38°.935	.366
2	51°.040	...	...	33.864	51°.320	.290
4	59°.137	...	...	38.258	59°.452	.315

The first four series, Tables X. to XIII., were made with one bulb to the air thermometer. A new bulb was now made, whose capacity was 192.0<sup>ccm.</sup>, that of the old being 201.98<sup>ccm.</sup>. The value of  $\frac{v}{V}$  for the new bulb was .0058. The values of  $k$  and  $\alpha$  were obtained as follows: —

	$\alpha$	$k$
June 8th	.00366790	753.876
June 22d	.00366977	753.805
June 25th	.00366779	753.837
Mean	.0036685	753.84

This value of  $\alpha$  is calculated with the old coefficient for glass. The new would have given .0036717.

TABLE XI.—SECOND SERIES, NOVEMBER 20–21, 1877.

Relative Weight.	Barometer corrected to 0° C.	Difference of Columns reduced to 0°	H	H - N'	$\frac{V}{e} \frac{H}{1+\gamma}$	$\frac{\delta}{H} \frac{a}{c}$	T Air Ther- mometer.	V 6168.	V 6166.	P 6167.	Tempera- ture by Göttsch.	Tempera- ture by Göttsch.
2	.....	-27.28	.....	.....	...	...	0	114.94	21.09	6.128	+0.50	0
8	773.00	- 6.84	706.16	16.49	4.09	5.28	7° 581	248.66	123.10	10.282	8.121	7° 089
2	772.78	+16.72	789.50	89.83	4.22	5.43	16° 234	400.52	238.60	14.986	16.78	16° 395
2	772.82	48.27	820.59	70.92	4.35	5.68	27° 755	602.60	392.65	21.246	28.31	27° 982
2	772.21	50.25	822.46	72.79	4.36	5.69	28° 449	615.10	402.29	21.628	29.01	28° 689
1	772.27	84.17	856.44	106.77	4.54	5.97	41° 070	834.99	....	23.489	41.53	41° 295
3	772.34	88.05	855.89	105.72	4.58	5.96	40° 678	828.87	....	23.259	41.23	40° 982
2	772.61	104.08	876.69	127.02	4.68	6.14	48° 514	....	....	32.516	49.01	48° 841
2	772.25	112.78	885.08	135.86	4.70	6.21	51° 706	....	....	34.208	52.17	51° 973
4	771.93	146.68	918.61	168.94	4.87	6.50	64° 206	....	....	40.943	64.47	64° 334
3	771.64	171.67	943.31	193.64	4.98	6.71	78° 402	....	....	45.890	73.61	78° 560
3	771.24	201.42	972.66	222.99	5.12	6.95	84° 344	....	....	51.767	84.43	84° 478
3	771.07	201.59	972.66	222.99	5.12	6.95	84° 344	....	....	51.770	84.43	84° 479
0	770.90	243.10	1014.00	264.83	5.32	7.31	99° 781	....	....	60.064	....	99° 880
0	770.71	242.12	1012.83	263.16	5.32	7.30	99° 846	....	....	....	99.26	99° 350
..	.....	.....	.....	.....	...	...	100° 000	....	....	60.156	99.83	....

N' = 749.67 mm.

TABLE XII. — THIRD SERIES, JANUARY 25, 1878.

Relative Weight.	Barometer reduced to 0°	Difference of Columns reduced to 0°	H	H - N'	$\frac{v}{\bar{v}} \frac{H}{1 + \gamma z}$	$H \frac{b}{a}$	Air Thermometer.	$\bar{v}$ 613.	$\bar{v}$ 616.	Gelsler.	Temperature by Gelsler.
1	764.198	-17.644	746.549	.....	8.94	...	0	115.50	21.44	+0.60	0
1	763.00	- 2.69	760.40	9.91	8.99	5.19	5° 114	205.80	90.84	....	....
1	763.06	- 0.63	762.43	11.94	4.00	5.21	5° 865	218.60	99.87	....	....
1	762.87	+ 11.96	774.83	24.84	4.06	5.31	10° 451	299.94	162.17	11.12	10° 58
1	762.82	34.09	798.91	46.42	4.18	5.49	18° 628	443.14	271.18	19.80	18° 82
1	762.89	54.47	817.36	66.87	4.29	5.65	26° 207	576.52	372.70	26.91	26° 48
1	762.89	62.19	825.08	74.59	4.30	5.72	28° 067	626.57	410.98	29.73	29° 31
1	762.83	88.27	851.10	100.61	4.43	5.98	38° 706	794.08	.....	89.32	38° 96
1	762.82	87.16	849.98	99.49	4.42	5.92	38° 288	787.86	.....	38.95	38° 59

N = 750.49.

TABLE XIII.—FOURTH SERIES, FEBRUARY 11, 1878.

Relative Weight.	Barometer reduced to 0°	Difference of Columns reduced to 0°	H	H - A'	$\frac{H}{1 + \gamma t}$	$H \frac{1}{a}$	T Air Thermometer.	V 6166.	V 6166.	V 6166.	Gelaser.	Temperature by Gelaser.
3	755.810	-8.737	746.578	-8.985	4.007	....	0° 008	21.21	6.202	115.50	+0.60	0
3	755.424	+0.611	756.085	5.447	4.039	5.156	8° 489	67.72	13.786	176.30	....	.....
2	755.846	1.600	756.946	6.358	4.042	5.162	8° 825	71.98	14.561	182.78	....	.....
3	755.274	11.665	766.939	16.851	4.095	5.289	7° 521	122.29	22.614	247.85	....	.....
3	755.250	12.792	768.042	17.464	4.097	5.246	7° 927	127.29	23.424	254.88	8.56	8° 01
4	755.222	25.536	780.758	30.170	4.169	5.857	12° 634	190.71	33.793	337.90	13.81	12° 79
4	755.495	40.863	796.358	45.770	4.241	5.479	18° 405	268.20	46.404	489.43	19.11	18° 63
4	755.444	58.882	814.326	68.788	4.386	5.909	25° 060	356.86	60.841	555.71	25.72	25° 28
3	755.481	71.852	827.383	76.745	4.390	5.733	29° 875	421.28	71.204	640.19	30.55	30° 14
3	755.497	71.365	826.862	76.274	4.386	5.785	29° 700	418.61	70.881	636.79	30.35	29° 94
4	755.928	94.718	850.641	100.053	4.519	5.929	38° 522	....	....	791.26	36.15	38° 80
5	755.626	258.768	1015.384	264.796	5.397	7.321	99° 840	....	....	....	96.813	99° 84
3	755.360	-8.748	746.617	-4.029	-4.007	....	-0° 008	....	....	....	....	.....

A' = 750.588 mean value before and after experiments.

The value  $\alpha = .00366767$  as obtained on the same day was used in this calculation.

TABLE XIV. — FIFTH SERIES, JUNE 8, 1878.

Weight for Air Ther- mome- ter.	Barometer reduced to 0°	Difference of Columns reduced to 0°	H	$H - N$	$\frac{v}{V} \frac{H}{1 + \gamma t}$	$\frac{b}{a} \frac{H}{1 + \gamma t}$	$\frac{b}{a}$	T Air Ther- mometer.	$\bar{V}$ 6165.	$\bar{V}$ 6163.	$\bar{V}$ Standard No. 104.	$\bar{V}$ Shortened Column.	Gelstier.	Temper- ature by Kew Stand- ard.	Temper- ature by Gelstier.	$\Delta$ Kew.	$\Delta$ Gelstier.
2	750.819	-1.004	749.815	-4.025	4.061	5.281	0° 014		7.054	115.98	32.78	.....	+0.80	0	0	-01	-01
2	749.710	21.904	771.614	17.774	4.164	5.348	8° 085		24.589	257.14	47.23	.....	.....	8° 04	.....	+01	.....
2	749.612	80.625	780.287	26.397	4.208	5.420	11° 209		31.445	312.53	52.91	62.86	.....	11° 20	.....	-01	.....
1	749.281	39.880	789.161	35.321	4.253	5.493	14° 498		38.594	370.22	58.84	106.67	15.155	14° 50	14° 65	.00	+15
2	748.986	48.069	797.075	43.235	4.298	5.546	17° 412		45.008	421.92	64.09	146.16	18.12	17° 48	17° 63	+02	+22
2	747.814	57.014	804.828	50.988	4.332	5.680	20° 270		51.277	472.32	69.32	184.54	21.00	20° 34	20° 53	+07	+26
2	747.530	74.320	821.850	68.010	4.418	5.785	26° 546		64.980	582.14	80.55	268.04	27.25	26° 59	26° 81	+04	+26
2	747.422	87.619	835.041	81.201	4.485	5.966	31° 412		75.485	667.40	89.29	333.17	32.14	31° 45	31° 73	+04	+32
1	747.082	108.744	855.826	101.986	4.598	6.211	39° 088		.....	801.76	103.06	435.58	39.80	39° 11	39° 44	+02	+35
2	747.008	139.450	886.458	132.618	4.754	6.423	50° 407		.....	.....	123.44	.....	50.99	50° 46	50° 70	+05	+29
2	746.816	164.446	911.292	157.422	4.890	7.346	59° 587		.....	.....	189.87	.....	59.99	59° 60	59° 76	+01	+16
2	746.826	272.075	1018.901	265.061	5.468	.....	99° 513		.....	.....	.....	.....	.....	.....	.....	.....	.....

TABLE XV.—SIXTH SERIES, JUNE 22, 1878.

Relative Weight.	Barometer reduced to 0°	Difference of Columns reduced to 0°	H	$H - h'$	$\frac{H}{V \frac{1}{1+\gamma t}}$	$H \frac{b}{a}$	T Air Thermometer.	V 6165.	V 6166.	Kew No. 104.	V 6166.	Y Gelshar.	Temperature by Kew Stand. Gelshar.	Temperature by Kew Stand. Gelshar.	$\Delta$ Kew.	$\Delta$ Gelshar.
1	750.411	-0.628	749.788	-4.057	4.029	....	-0° 010	7.040	115.88	32.75	21.63	+0.60	0	0	+0.01	+0.01
1	750.843	45.692	796.085	42.195	4.269	5.476	17° 021	44.186	415.88	68.48	249.81	17.71	17° 10	17° 22	+0.08	+0.20
1	750.220	82.985	838.155	79.315	4.448	5.774	30° 705	74.011	655.65	88.08	438.02	31.48	30° 79	31° 02	+0.09	+0.31
1	750.170	108.407	858.577	104.787	4.575	5.986	40° 068	....	819.68	104.98	....	40.79	40° 16	40° 43	+0.07	+0.34
1	749.914	186.270	886.184	182.344	4.721	6.212	50° 292	....	....	123.26	....	50.87	50° 36	50° 57	+0.07	+0.28
1	750.127	173.486	928.613	169.778	4.919	6.531	64° 144	....	....	148.105	....	64.515	64° 19	64° 30	+0.05	+0.17
1	749.994	190.045	940.039	186.199	5.004	6.665	70° 227	....	....	159.08	....	70.555	70° 27	70° 37	+0.04	+0.14
1	750.653	212.443	963.096	209.256	5.127	6.987	78° 775	....	....	174.31	....	78.97	78° 77	78° 84	+0.00	+0.07
1	750.923	281.446	982.869	228.529	5.229	7.024	85° 924	....	....	187.03	....	86.01	85° 85	85° 98	+0.07	+0.01
1	751.304	268.154	1019.458	265.618	5.425	7.351	99° 700	....	....	211.88	....	99.68	99° 68	99° 68	+0.02	+0.02

It now remains to determine from these experiments the most probable values of the constants in the formula, comparing the air with the mercurial thermometer. The formula is, as we have found,

$$t = T - at(t' - t)(b - t);$$

but I have generally used it in the following form:—

$$t = C'V - t_0 - mt(100 - t)(1 - n(100 + t)),$$

$$t = C'V - t'_0 - mt(40 - t)(1 - n(40 + t)).$$

And the following relations hold among the constants:—

$$C = C'(1 + m(60 - 8400n)), \text{ nearly,}$$

$$a = mn,$$

$$b = \frac{1}{n} - 100^\circ,$$

$$T = C'V - t_0,$$

$$t_0 = t'_0 \frac{C}{C'}.$$

In these formulæ  $t$  is the temperature on the air thermometer;  $V$  is the volume of the stem of the mercurial thermometer, as determined from the calibration and measured from any arbitrary point; and  $C'$ ,  $t_0$ ,  $m$ , and  $n$  are constants to be determined.

The best way of finding these is by the method of least squares.  $C'$  must be found very exactly;  $t_0$  is only to be eliminated from the equations;  $m$  must be found within say ten per cent, and  $n$  need only be determined roughly. To find them only within these limits is a very difficult matter.

#### *Determination of $n$ .*

As this constant needs a wide range of temperatures to produce much effect, it can only be determined from thermometer No. 6167, which was of the same glass as 6163, 6165, and 6166. It is unfortunate that it was broken on November 21, and so we only have the experiments of the first and second series. From these I have found  $n = .008$  nearly. This makes  $b = 233^\circ$ , which is not very far from the values found before from experiments above  $100^\circ$  by Regnault on ordinary glass.\*

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\* Some experiments with Baudin thermometers at high temperatures have given me about  $240^\circ$ ,—a remarkable agreement, as the point must be uncertain to  $10^\circ$  or more.



*Determination of C and m.*

I shall first discuss the determination of these for thermometers Nos. 6163, 6165, and 6166, as these were the principal ones used.

As No. 6163 extended from  $0^\circ$  to  $40^\circ$ , and the others only from  $0$  to  $30^\circ$ , it was thought best to determine the constants for this one first, and then find those for 6165 and 6166 by comparison. As this comparison is deduced from the same experiments as those from which we determine the constants of 6163, very nearly the same result is found as if we obtained the constants directly by comparison with the air thermometer.

The constants of 6163 can be found either by comparison with 6167, or by direct comparison with the air thermometer. I shall first determine the constants for No. 6167.

The constants  $C$  and  $t_0$  for this thermometer were found directly by observation of the  $0^\circ$  and  $100^\circ$  points; and we might assume these, and so seek only for  $m$ . In other words, we might seek only to express the difference of the thermometers from the air thermometer by a formula. But this is evidently incorrect, seeing that we thus give an infinite weight to the observations at the  $0$  and  $100^\circ$  points. The true way is obviously to form an equation for each temperature, giving each its proper weight. Thus from the first series we find for No. 6167,—

Weight.	Equations of condition.
4	$0 = 6.147 C - t_0,$
4	$17^\circ.427 = 15.685 C - t_0 - 930 m,$
4	$23^\circ.793 = 19.157 C - t_0 - 1140 m,$
&c.	&c. &c.
5	$100^\circ = 60.156 C - t_0,$

which can be solved by the method of least squares. As  $t_0$  is unimportant, we simply eliminate it from the equations. I have thus found,—

Weight.			
1	Nov. 14	$C = 1.85171$	$m = .000217$
2	Nov. 20, 21	$C = 1.85127$	$m = .000172$
	Mean	$C = 1.85142$	$m = .000187$

The difference in the values of  $m$  is due to the observations not being so good as were afterwards obtained. However, the difference only signifies about  $0^\circ.03$  difference from the mean at the  $50^\circ$  point. After November 20 the errors are seldom half of this, on account of the greater experience gained in observation.

The ratio of  $C$  for 6167 and 6163 is found in the same way.

Weight.		
1	Nov. 14	.0310091
2	Nov. 20	.0309846
	Mean	.0309928

Hence for 6163 we have in this way

$$C = .057381 \quad C' = .056995 \quad m = .000187.$$

By direct comparison of No. 6163 with the air thermometer, we find the following.

Date.	Weight	$C$ .	$m$ .
Nov. 14	1	.056920	.000239
Nov. 20	2	.056985	.000166
Jan. 25	3	.056986	.000226
Feb. 11	4	.056997	.000155
June 8	3	.056961	.000071
June 22	2	.056959	.000115
Mean		.056976 $\pm$ .000004	.000154 $\pm$ .000010

The values of  $C'$  agree with each other with great exactness, and the probable error is only  $\pm 0.003$  C. at the  $40^\circ$  point.

The great differences in the values of  $m$ , when we estimate exactly what they mean in degrees, also show great exactness in the experiments. The mean value of  $m$  indicates a difference of only  $0.05$  between the mercurial and air thermometer at the  $20^\circ$  point, the  $0^\circ$  and  $40^\circ$  points coinciding. The probable error of  $m$  in degrees is only  $\pm 0.003$  C.

There is one more method of finding  $m$  from these experiments; and that is by comparing the values of  $C'$  with No. 6167, the glass of 6167 being supposed to be the same as that of 6163.

We have the formula

$$C = C' (1 + 34.8 m).$$

Hence

$$m = \frac{C - C'}{34.8 C'}.$$

We thus obtain the following results:—

Date.	Weight.	Value of $m$ .
Nov. 14	1	.000236
Nov. 20	2	.000218
Jan. 25	3	.000217
Feb. 11	4	.000197
June 8	3	.000215
June 22	2	.000216
Mean		.000213

The results for  $m$  are then as follows:—

From direct comparison of No. 6167 with the air thermometer	.000187
From “ “ “ No. 6163 “ “ “	.000154
From comparison of No. 6163 with No. 6167	.000218

The first and last are undoubtedly the most exact numerically, but they apply to No. 6167, and are also, especially the first, derived from somewhat higher temperatures than the  $20^\circ$  point, where the correction is the most important. The value of  $m$ , as determined in either of these ways, depends upon the determination of a difference of temperature amounting to  $0^\circ.30$ , and hence should be quite exact.

The value of  $m$ , as obtained from the direct comparison of No. 6163 with the air thermometer, depends upon the determination of a difference of about  $0^\circ.05$  between the mercurial and the air thermometer. At the same time, the comparison is direct, the temperatures are the same as we wish to use, and the glass is the same. I have combined the results as follows:—

$m$ from No. 6167	.000200
$m$ “ 6163	.000154
Mean	.00018*

It now remains to deduce from the tables the ratios of the constants for the different thermometers.

The proper method of forming the equations of condition are as follows, applying the method to the first series:—

Weight.	
4	$21.25 C_{III} = 115.33 C_I - v_0$
4	$255.80 C_{III} = 422.84 C_I - v_0$
4	$341.05 C_{III} = 534.71 C_I - v_0$
5	$431.71 C_{III} = 653.49 C_I - v_0$

where  $C_{III}$  is the constant for No. 6166,  $C_I$  is that for No. 6163, and  $v_0$  is a constant to be eliminated. Dividing by  $C_I$ , the equations can be solved for  $\frac{C_{III}}{C_I}$ . The following table gives the results.

---

\* See Appendix to Thermometry, where it is finally thought best to reject the value from No. 6167 altogether.

TABLE XVI. — RATIOS OF CONSTANTS.

Date.	Weight.	$\frac{6163}{6167}$	$\frac{6166}{6167}$	$\frac{6166}{6168}$	$\frac{6166}{6168}$	$\frac{6166}{6168}$
Nov. 14	1	.031009	.040658	1.3111	....	....
Nov. 20	2	.030985	.040670	1.3128	....	....
Jan. 25	8	....	....	1.3122	....	....
Feb. 11	4	....	....	1.3115	8.0588	6.1449
June 8	8	....	....	1.3108	8.0605	6.1469
June 22	2	....	....	1.3122	8.0588	6.1428
Mean		$\left\{ \begin{array}{l} .030993 \\ \pm .00005 \end{array} \right.$	$\left\{ \begin{array}{l} .040666 \\ \pm .000008 \end{array} \right.$	$\left\{ \begin{array}{l} 1.31175 \\ \pm .0004 \end{array} \right.$	$\left\{ \begin{array}{l} 8.0594 \\ \pm .0002 \end{array} \right.$	$\left\{ \begin{array}{l} 6.1451 \\ \pm .0004 \end{array} \right.$

From these we have the following, as the final most probable results: —

$$\begin{aligned} C_{II} &= 8.0601 C_p, \\ C_{III} &= 1.31175 C_p, \\ C_I &= .031003 C_{IV}, \\ C_{II} &= .24991 C_{IV}, \\ C_{III} &= .040661 C_{IV}, \end{aligned}$$

of which the last three are only used to calculate the temperatures on the mercurial thermometer, and hence are of little importance in the remainder of this paper.

The value of  $C'$  which we have found for the old value of the coefficient of expansion of glass was

$$C' = .056976;$$

and hence, corrected to the new coefficient, it is, as I have shown,

$$C_I = .056962.$$

Hence,

$$\begin{aligned} C_{II} &= .45912, \\ C_{III} &= .074720. \end{aligned}$$

And we have finally the three following equations to reduce the thermometers to temperatures on the air thermometer: —

Thermometer No. 6163:

$$T = .056962 V' - t_0' - .00018 T (40 - T) (1 - .003 (T + 40)).$$

Thermometer No. 6165:

$$T = .45912 V'' - t_0'' - .00018 T (T - 40) (1 - .003 (T + 40)).$$

Thermometer No. 6166:

$$T = .074720 V''' - t_0''' - .00018 T(T - 40) (1 - .003 (T + 40));$$

where  $V'$ ,  $V''$ , and  $V'''$  are the volumes of the tube obtained by calibration;  $t_0'$ ,  $t_0''$ , and  $t_0'''$  are constants depending on the zero point, and of little importance where a difference of temperature is to be measured; and  $T$  is the temperature on the air thermometer.

On the mercurial thermometer, using the  $0^\circ$  and  $100^\circ$  points as fixed, we have the following by comparison with No. 6167:—

$$\text{Thermometer No. 6163; } t = .057400 V - t_0;$$

$$\text{Thermometer No. 6165; } t = .46265 V - t_0;$$

$$\text{Thermometer No. 6166; } t = .075281 V - t_0.$$

### *The Kew Standard.*

The Kew standard must be treated separately from the above, as the glass is not the same. This thermometer has been treated as if its scale was arbitrary.

In order to have variety, I have merely plotted all the results with this thermometer, including those given in the Appendix, and drawn a curve through them. Owing to the thermometer being only divided to  $\frac{1}{2}^\circ$  F., the readings could not be taken with great accuracy, and so the results are not very accordant; but I have done the best I could, and the result probably represents the correction to at least  $0^\circ.02$  or  $0^\circ.03$  at every point.

### (d) Reduction to the Absolute Scale.

The correction to the air thermometer to reduce to the absolute scale has been given by Joule and Thomson, in the Philosophical Transactions for 1854; but as the formula there used is not correct, I have recalculated a table from the new formula used by them in their paper of 1862.

That equation, which originated with Rankine, can be placed in the form

$$\frac{p}{\mu} v = C (1 - m \frac{\mu_0}{\mu^2} D);$$

where  $p$ ,  $v$ , and  $\mu$  are the pressure, volume, and absolute temperature of a given weight of the air;  $D$  is its density referred to air at  $0^\circ$  C. and 760<sup>mm</sup> pressure;  $\mu_0$  is the absolute temperature of the freezing point; and  $m$  is a constant which for air is  $0^\circ.33$  C.

For the air thermometer with constant volume

$$T = 100 \frac{p_t - p_0}{p_{100} - p_0};$$

$$\therefore T = (\mu - \mu_0) \left( 1 + m D \left( \frac{1}{\mu} - \frac{1}{\mu_{100}} \right) \right);$$

or, since  $D = 1$ ,

$$\mu - \mu_0 = T - .00088 T \frac{100 - T}{278 + T},$$

from which I have calculated the following table of corrections.

TABLE XVII.—REDUCTION OF AIR THERMOMETER TO ABSOLUTE SCALE.

$T$ Air Thermometer.	$\mu - \mu_0$ Absolute Temperature.	$\Delta$ or Correction to Air Thermometer.
0	0	0
10	9.9972	— .0028
20	19.9952	— .0048
30	29.9989	— .0061
40	39.9983	— .0067
50	49.9982	— .0068
60	59.9987	— .0063
70	69.9946	— .0054
80	79.9956	— .0044
90	89.9978	— .0022
100	100.000	0
200	200.087	+ .087
300	300.092	+ .092
400	400.157	+ .157
500	500.228	+ .228

It is a curious circumstance, that the point of maximum difference occurs at about the same point as in the comparison of the mercurial and air thermometers.

From the previous formula, and from this table of corrections, the following tables were constructed.

TABLE XVIII. — THERMOMETER No. 6163.

Reading in Millimeters on Stem.	Temperature on Mercurial Thermometer, 0 and 100° fixed.	Temperature on Mercurial Thermometer, 0 and 40° fixed by Air Thermometer.	Temperature on Air Thermometer.	Temperature on Absolute Scale from 0° C.	Reading in Millimeters on Stem.	Temperature on Mercurial Thermometer, 0 and 100° fixed.	Temperature on Mercurial Thermometer, 0 and 40° fixed by Air Thermometer.	Temperature on Air Thermometer.	Temperature on Absolute Scale from 0° C.
50	—°.923	—°.917	—°.911	—°.911	240	20.557	20.409	20.350	20.345
58.1	0	0	0	0	250	21.670	21.515	21.457	21.452
60	+°.217	+°.215	+°.214	+°.214	260	22.776	22.618	22.559	22.554
70	1.356	1.336	1.328	1.328	270	23.884	23.718	23.657	23.652
80	2.494	2.475	2.461	2.460	280	24.989	24.810	24.755	24.750
90	3.631	3.604	3.584	3.583	290	26.098	25.907	25.854	25.848
100	4.767	4.733	4.707	4.706	300	27.200	27.006	26.956	26.950
110	5.908	5.860	5.829	5.827	310	28.311	28.108	28.060	28.056
120	7.086	6.986	6.950	6.948	320	29.425	29.214	29.169	29.163
130	8.170	8.111	8.071	8.069	330	30.541	30.324	30.282	30.276
140	9.304	9.237	9.198	9.190	340	31.662	31.436	31.398	31.392
150	10.436	10.361	10.314	10.311	350	32.782	32.548	32.514	32.508
160	11.568	11.485	11.435	11.432	360	33.908	33.660	33.630	33.624
170	12.700	12.608	12.558	12.553	370	35.023	34.773	34.748	34.742
180	13.829	13.730	13.676	13.672	380	36.143	35.884	35.864	35.857
190	14.957	14.850	14.794	14.790	390	37.261	36.994	36.979	36.972
200	16.081	15.968	15.909	15.905	400	38.377	38.103	38.094	38.087
210	17.208	17.080	17.022	17.018	410	39.492	39.210	39.206	39.199
220	18.322	18.191	18.132	18.127	420	40.604	40.314	40.316	40.309
230	19.440	19.301	19.242	19.237					

TABLE XIX. — THERMOMETER No. 6165.

Reading in Millimeters on Stem.	Temperature on Mercurial Thermometer, 0 and 100° fixed.	Temperature on Mercurial Thermometer, 0 and 40° fixed by Air Thermometer.	Temperature on Air Thermometer.	Temperature on Absolute Scale from 0° C.	Reading in Millimeters on Stem.	Temperature on Mercurial Thermometer, 0 and 100° fixed.	Temperature on Mercurial Thermometer, 0 and 40° fixed by Air Thermometer.	Temperature on Air Thermometer.	Temperature on Absolute Scale from 0° C.
80	—°.464	—°.460	—°.457	—°.457	230	17.198	17.067	17.009	17.006
85	0	0	0	0	240	18.056	17.920	17.861	17.857
40	+°.463	+°.460	+°.457	+°.457	250	18.917	18.778	18.714	18.709
50	1.387	1.376	1.368	1.368	260	19.771	19.621	19.562	19.557
60	2.307	2.290	2.276	2.275	270	20.621	20.465	20.406	20.401
70	3.216	3.192	3.174	3.173	280	21.469	21.306	21.247	21.242
80	4.122	4.092	4.069	4.068	290	22.308	22.139	22.081	22.076
90	5.022	4.984	4.957	4.955	300	23.144	22.969	22.912	22.907
100	5.916	5.872	5.841	5.839	310	23.974	23.792	23.736	23.731
110	6.804	6.753	6.714	6.712	320	24.796	24.607	24.552	24.547
120	7.685	7.628	7.590	7.588	330	25.618	25.424	25.370	25.365
130	8.564	8.500	8.459	8.456	340	26.433	26.232	26.180	26.174
140	9.439	9.368	9.324	9.321	350	27.245	27.038	26.987	26.981
150	10.309	10.232	10.182	10.183	360	28.049	27.837	27.788	27.782
160	11.174	11.091	11.042	11.039	370	28.856	28.637	28.590	28.584
170	12.038	11.947	11.896	11.893	380	29.651	29.426	29.382	29.376
180	12.900	12.802	12.749	12.746	390	30.449	30.218	30.176	30.170
190	13.760	13.655	13.601	13.598	400	31.249	31.011	30.971	30.965
200	14.619	14.508	14.453	14.450	410	32.073	31.829	31.782	31.786
210	15.479	15.362	15.305	15.302	420	32.861	32.611	32.577	32.581
220	16.340	16.215	16.167	16.163					

TABLE XX. — THERMOMETER NO. 6166.

Reading in Millimeters on Stem.	Temperature on Mercurial Thermometer, 0 and 100° fixed.	Temperature on Mercurial Thermometer, 0 and 40° fixed.	Temperature on Air Thermometer.	Temperature on Absolute Scale from 0° C.	Reading in Millimeters on Stem.	Temperature on Mercurial Thermometer, 0 and 100° fixed.	Temperature on Mercurial Thermometer, 0 and 40° fixed.	Temperature on Air Thermometer.	Temperature on Absolute Scale from 0° C.
20	−.086	−.086	−.084	−.084	230	16.478	16.368	16.298	16.294
30	+.770	+.764	+.759	+.759	240	17.259	17.182	17.074	17.070
40	1.574	1.562	1.553	1.553	250	18.042	17.908	17.849	17.846
50	2.368	2.360	2.336	2.336	260	18.825	18.686	18.627	18.622
60	3.156	3.133	3.115	3.114	270	19.609	19.464	19.405	19.400
70	3.941	3.911	3.889	3.888	280	20.392	20.241	20.182	20.177
80	4.726	4.691	4.665	4.664	290	21.176	21.019	20.960	20.955
90	5.509	5.468	5.438	5.436	300	21.735	21.798	21.785	21.780
100	6.293	6.246	6.212	6.210	310	22.511	22.569	22.511	22.506
110	7.076	7.024	6.988	6.986	320	23.292	23.349	23.292	23.287
120	7.862	7.804	7.765	7.763	330	24.075	24.131	24.075	24.070
130	8.649	8.585	8.544	8.542	340	24.855	24.910	24.855	24.850
140	9.437	9.367	9.328	9.321	350	25.634	25.687	25.634	25.628
150	10.228	10.151	10.105	10.102	360	26.415	26.466	26.412	26.406
160	11.017	10.985	10.887	10.884	370	27.441	27.245	27.195	27.189
170	11.805	11.717	11.667	11.664	380	28.240	28.030	27.982	27.976
180	12.589	12.496	12.444	12.441	390	29.080	28.814	28.768	28.762
190	13.370	13.271	13.217	13.214	400	29.819	29.597	29.550	29.544
200	14.148	14.048	13.988	13.984	410	30.603	30.381	30.339	30.333
210	14.923	14.812	14.756	14.752	420	31.396	31.162	31.128	31.117
220	15.699	15.583	15.526	15.522	430	32.189	31.950	31.914	31.908

In using these tables a correction is of course to be made should the zero point change.

TABLE XXI. — CORRECTION OF KEW STANDARD TO THE ABSOLUTE SCALE.

Temperature C.	Correction in Degrees C.
0°	0
10°	−.03
20°	−.06
30°	−.06
40°	−.07
50°	−.07
60°	−.06
70°	−.04
80°	−.02
90°	−.01
100°	0



## Appendix to Thermometry.

The last of January, 1879, Mr. S. W. Holman, of the Massachusetts Institute of Technology, came to Baltimore to compare some thermometers with the air thermometer; and by his kindness I will give here the results of the comparison which we then made together.

As in this comparison some thermometers made by Fastré in 1851 were used, the results are of the greatest interest.

The tables are calculated with the newest value for the coefficient of expansion of glass. The calibration of all the thermometers, except the two by Casella, has been examined, and found good. The Casella thermometers had no reservoir at the top, and could not thus be readily calibrated after being made. The Geissler also had none, but I succeeded in separating a column.

The absence of a reservoir at the top should immediately condemn a standard, for there is no certainty in the work done with it.

TABLE XXII.—SEVENTH SERIES.

Air Thermometer.	Original Readings.					Reduced Readings.				
	6168.	7884 Baudin.	Kew Standard No. 104.	82874 Casella.	Geissler.	6168 Reduced to Air Thermometer.	7884 Baudin.	Kew Standard No. 104.	82874 Casella.	Geissler.
0	*58.88	—11	82.68	+20	+69	0	0	0	0	0
†.48	68.5	....	88.60	.71	....	.52	....	.52	.51	....
6.08	118.0	....	43.65	6.38	....	6.08	....	6.11	6.18	....
12.68	171.55	12.59	55.47	12.91	13.42	12.65	12.78	12.68	12.70	12.82
20.49	242.0	20.48	69.55	20.77	21.29	20.49	20.63	20.57	20.56	20.74
24.55	278.8	24.50	76.90	24.80	25.33	24.54	24.66	24.61	24.59	24.81
29.51	328.9	29.49	85.88	29.80	30.32	29.52	29.66	29.61	29.58	29.88
39.45	413.1	39.48	108.72	39.76	40.22	39.47	39.62	39.53	39.54	39.80
89.15	410.7	39.15	108.28	39.48	89.98	89.20	89.34	89.26	89.26	89.66
51.17	....	51.10	124.84	51.49	51.83	....	51.32	51.29	51.26	51.49
61.12	....	61.05	142.73	61.47	61.69	....	61.29	61.24	61.28	61.41
70.74	....	70.57	159.87	71.00	71.14	....	70.83	70.78	70.76	70.92
80.09	....	79.74	176.50	80.31	80.25	....	80.02	80.04	80.06	80.10
80.89	....	80.15	177.23	80.74	80.66	....	80.43	80.44	80.49	80.51
89.95	....	89.63	194.35	90.22	90.11	....	89.93	89.97	89.97	90.03
89.92	....	89.69	194.22	90.18	90.06	....	89.89	89.90	89.93	89.98
100.00	....	99.69	212.87	100.06	99.32	....	100.00	100.00	100.00	100.00

\* The original readings in ice were 58.68 and 58.45, to which .15 was added to allow for the pressure of water in the comparator. This, of course, gives the same final result as if .15 were subtracted from each of the other temperatures. No correction was made to the others.

† Probably some error of reading.

TABLE XXIII.—EIGHTH SERIES.

Air Thermometer.	Original Readings.					Reduced Readings.				
	6163.	376 Fastré.	7316 Baudin.	368 Fastré.	3225 Casella.	6163 Reduced to Air Thermometer.	376 Fastré.	7316 Baudin.	368 Fastré.	3225 Casella.
0	*58.60	111.8	—23	87.6	32.80	0	0	0	0	0
8.67	90.7	130.0	....	106.25	39.35	3.61	3.64	....	3.64	3.65
11.55	161.6	170.9	11.40	147.2	58.70	11.56	11.60	11.64	11.62	11.63
20.72	243.7	217.9	20.59	194.2	70.15	20.70	20.75	20.84	20.80	20.79
32.19	347.4	276.9	32.09	253.2	90.80	32.17	32.24	32.34	32.28	32.29
39.86	411.85	318.85	39.26	290.1	103.68	39.86	39.43	39.52	39.48	39.45
50.71	....	372.0	50.57	248.2	123.65	....	50.75	50.84	50.80	50.57
60.10	....	420.0	59.92	396.45	140.80	....	60.10	60.19	60.21	60.12
73.82	....	490.6	73.59	466.85	165.68	....	73.84	73.87	73.93	73.97
86.50	....	555.25	86.16	531.22	188.20	....	86.48	86.51	86.56	86.56
....	....	550.2	85.21	525.95	186.42	....	86.45	85.50	85.45	85.51
100.00	....	624.98	99.70	600.68	212.45	....	100.00	100.00	100.00	100.00

From these tables we would draw the inference that No. 6163 represents the air thermometer with considerable accuracy. At the same time, both tables would give a smaller value of  $m$  than I have used, and not very far from the value found before by *direct* comparison, namely, .00015.

The difference from using  $m = .00018$  would be a little over  $0^{\circ}.01$  C. at the  $20^{\circ}$  point.

All the other thermometers stand *above* the air thermometer, between  $0$  and  $100^{\circ}$ , by amounts ranging between about  $0^{\circ}.05$  and  $0^{\circ}.35$  C., *none* standing below. Indeed, no table has ever been published showing any thermometer standing *below* the air thermometer between  $0$  and  $100^{\circ}$ . By inference from experiments above  $100^{\circ}$  on crystal glass by Regnault, thermometers of this glass should stand below, but it never seems to have been proved by direct experiment. The Fastré thermometers are probably made of this glass, and my Baudins certainly contain lead; and yet these stand above, though only to a small amount, in the case of the Fastré's.

The Geissler still seems to retain its pre-eminence as having the greatest error of the lot.

The Baudin thermometers agree well together, but are evidently made from another lot of glass from the No. 6167 used before. These last two depart less from the air thermometer. The explanation is plain, as Baudin had manufactured more than one thousand ther-

\* See note on preceding page.

mometers between the two, and so had probably used up the first stock of glass. And even glass of the same lot differs, especially as Regnault has shown that the method of working it before the blow-pipe affects it very greatly.

It is very easy to test whether the calorimeter thermometers are of the same glass as any of the others, by testing whether they agree with No. 6163 throughout the whole range of  $40^{\circ}$ . The difference in the values of  $m$  for the two kinds of glass will then be about .003 of the difference between them at  $20^{\circ}$ , the 0 and  $40^{\circ}$  points agreeing. The only difficulty is in calibrating or reading the  $100^{\circ}$  thermometers accurately enough.

The Baudin thermometers were very well calibrated, and were graduated to  $\frac{1}{10}^{\circ}$  C., and so were best adapted to this kind of work. Hence I have constructed the following tables, making the 0 and  $40^{\circ}$  points agree.

TABLE XXIV.—COMPARISON OF 6163 AND THE BAUDIN STANDARDS.

6163 Mercurial 0 and $40^{\circ}$ fixed.	7334.*	Difference.	6163 Mercurial 0 and $40^{\circ}$ fixed.	7316.*	Difference.
0	0	0	0	0	0
12.699	12.678	+.026	11.609	11.584	+.025
20.547	20.558	— .006	20.762	20.746	+.016
24.604	24.567	+.037	32.203	32.211	— .008
29.564	29.550	+.014	39.358	39.358	0
39.337	39.387	0			

Taking the average of the two, it would seem that No. 6163 stood about .015 higher than the mean of 7334 and 7316 at the  $20^{\circ}$  point, or 6163 has a higher value of  $m$  by .000045 than the others.

These differ about .17 from the air thermometer at  $40^{\circ}$ , which gives the value of  $m$  about .000104. Whence  $m$  for 6163 is .00015, as we have found before by direct comparison with the air thermometer.

I am inclined to think that the former value, .00018, is too large, and to take .00015, which is the value found by direct comparison, as the true value. As the change, however, only makes at most a difference of  $0^{\circ}.01$  at any one point, and as I have already used the previous value in all calculations, I have not thought it worth while to go over all my work again, but will refer to the matter again in the final results, and then reduce the final results to this value.

\* A correction of  $0^{\circ}.01$  was made to the zero points of these thermometers on account of the pressure of the water.

## III.—CALORIMETRY.

(a) *Specific Heat of Water.*

The first observers on the specific heat of water, such as De Luc, completed the experiment with a view of testing the thermometer; and it is curious to note that both De Luc and Flaugergues found the temperature of the mixture less than the mean of the two equal portions of which it was composed, and hence the specific heat of cold water *higher* than that of warm.

The experiments of Flaugergues were apparently the best, and he found as follows: \*—

3 parts of water at 0°	and 1 part at 80° R.	gave 19°.86 R.
2 parts of       "       "	2 parts       "       "	39°.81 R.
1 part of       "       "	3 parts       "       "	59°.87 R.

But it is not at all certain that any correction was made for the specific heat of the vessel, or whether the loss by evaporation or radiation was guarded against.

The first experiments of any accuracy on this subject seem to have been made by F. E. Newmann in 1831.† He finds that the specific heat of water at the boiling point is 1.0127 times that at about 28° C. (22° R.).

The next observer seems to have been Regnault,‡ who, in 1840, found the mean specific heat between 100° C. and 16° C. to be 1.00709 and 1.00890 times that at about 14°.

But the principal experiments on the subject were published by Regnault in 1850,§ and these have been accepted to the present time. It is unfortunate that these experiments were all made by mixing water above 100° with water at ordinary temperatures, *it being assumed that water at ordinary temperatures changed little, if any.* An interpolation formula was then found to represent the results; and *it was assumed* that the same formula held at ordinary temperature, or even as low as 0° C. It is true that Regnault experimented on the subject at points around 4° C. by determining the specific heat of lead in water at various temperatures; but the results were not of sufficient accuracy to warrant any conclusions except that the variation was not great.

\* Gehler, Phys. Wörterbuch, i. 641.

† Pogg. Ann., xxiii. 40.

‡ Ibid., li. 72.

§ Pogg. Ann., lxxix. 241; also, Rel. d. Exp., i. 729.

Boscha has attempted to correct Regnault's results so as to reduce them to the air thermometer; but Regnault, in *Comptes Rendus*, has not accepted the correction, as the results were already reduced to the air thermometer.

Hirn (*Comptes Rendus*, lxx. 592, 831) has given the results of some experiments on the specific heat of water at low temperatures, which give the absurd result that the specific heat of water increases about six or seven per cent between zero and  $13^{\circ}$ ! The method of experiment was to immerse the bulb of a water thermometer in the water of the calorimeter, until the water had contracted just so much, when it was withdrawn. The idea of thus giving equal quantities of heat to the water was excellent, but could not be carried into execution without a great amount of error. Indeed, experiments so full of error only confuse the physicist, and are worse than useless.

The experiments of Jamin and Amaury, by the heating of water by electricity, were better in principle, and, if carried out with care, would doubtless give good results. But no particular care seems to have been taken to determine the variation of the resistance of the wire with accuracy, and the measurement of the temperature is passed over as if it were a very simple, instead of an immensely difficult matter. Their results are thus to be rejected; and, indeed, Regnault does not accept them, but believes there is very little change between  $5^{\circ}$  and  $25^{\circ}$ .

In Poggendorff's *Annalen* for 1870 a paper by Pfaundler and Platner appeared, giving the results of experiments around  $4^{\circ}$  C., and deducing the remarkable result that water from 0 to  $10^{\circ}$  C. varied as much as twenty per cent. in specific heat, and in a very irregular manner,—first decreasing, then increasing, and again decreasing. But soon after another paper appeared, showing that the results of the previous experiments were entirely erroneous.

The new experiments, which extended up to  $13^{\circ}$  C., seemed to give an increase of specific heat up to about  $6^{\circ}$ , after which there was apparently a decrease. It is to be noted that Geissler's thermometers were used, which I have found to depart more than any other from the air thermometer.

But as the range of temperature is very small, the reduction to the air thermometer will not affect the results very much, though it will somewhat decrease the apparent change of specific heat.

In the *Journal de Physique* for November, 1878, there is a notice of some experiments of M. von Münchhausen on the specific heat of

water. The method was that of mixture in an open vessel, where evaporation might interfere very much with the experiment. No reference is made to the thermometer, but it seems not improbable that it was one from Geissler; in which case the error would be very great, as the range was large, and reached even up to 70° C. The error of the Geissler would be in the direction of making the specific heat increase more rapidly than it should. The formula he gives for the specific heat of water at the temperature  $t$  is

$$1 + .000302 t.$$

Assuming that the thermometer was from Geissler, the formula, reduced to the air thermometer, would become approximately

$$1 - .00009 t + .0000015 t^2.$$

Had the thermometer been similar to that of Recknagel, it would have been  $1 + .000045 t + .000001 t^2$ .

It is to be noted that the first formula would actually give a decrease of specific heat at first, and then an increase.

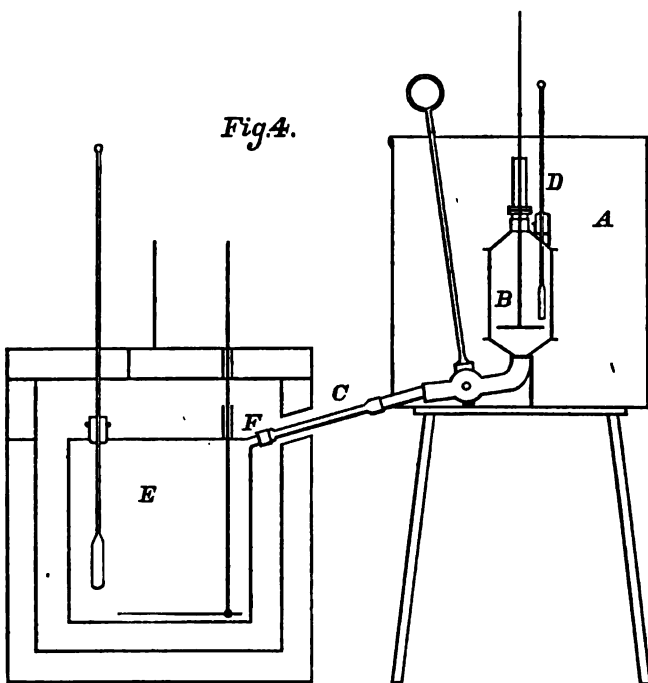
As all these results vary so very much from each other, we can hardly say that we know anything about the specific heat of water between 0 and 100°, though Regnault's results above that temperature are probably very nearly correct.

It seems to me probable that my results with the mechanical equivalent apparatus give the variation of the specific heat of water with considerable accuracy; indeed, far surpassing any results which we can obtain by the method of mixture. It is a curious result of those experiments, that at low temperatures, or up to about 30° C., the specific heat of water is about constant *on the mercurial thermometer* made by Baudin, but *decreases to a minimum at about 30° when the reduction is made to the air thermometer or the absolute scale*, or, indeed, the Kew standard.

As this curious and interesting result depends upon the accurate comparison of the mercurial with the air thermometer, I have spent the greater part of a year in the study of the comparison, but have not been able to find any error, and am now thoroughly convinced of the truth of this decrease of the specific heat. But to make certain, I have instituted the following independent series of investigations on the specific heat of water, using, however, the same thermometers.

The apparatus is shown in Fig. 4. A copper vessel,  $A$ , about 20<sup>cm</sup>.

in diameter and 23<sup>cm</sup>. high, rests upon a tripod. In its interior is a three-way stopcock, communicating with the small interior vessel *B*, the vessel *A*, and the vulcanite spout *C*. By turning it, the vessel *B* could be filled with water, and its temperature measured by the thermometer *D*, after which it could be delivered through the spout into the calorimeter. As the vessel *B*, the stopcock, and most of the spout, were within the vessel *A*, and thus surrounded by water, and as the vulcanite tube was very thin, the water could be delivered into the



calorimeter without appreciable change of temperature. The proof of this will follow later.

The calorimeter, *E*, was of very thin copper, nickel-plated very thinly. A hole in the back at *F* allowed the delivery spout to enter, and two openings on top admitted the thermometers. A wire attached to a stirrer also passed through the top. The calorimeter had a capacity of about three litres, and weighed complete about 388.3 grammes. Its calorific capacity was estimated at 35.4 grammes. It rested on three vulcanite pieces, to prevent conduction to the jacket.

Around the calorimeter on all sides was a water-jacket, nickel-plated on its interior, to make the radiation perfectly definite.

The calorific capacity of the thermometers, including the immersed stem and the mercury of the bulb, was estimated as follows:  $14^{\text{mm}}$  of stem weighed about  $3.8^{\text{gr}}$ , and had a capacity of  $.8^{\text{gr}}$ ;  $10^{\text{gr}}$  of mercury had a capacity of  $.3^{\text{gr}}$ ; total,  $1.1^{\text{gr}}$ .

Often the vessel *B* was removed, and the water allowed to flow directly into the calorimeter.

The following is the process followed during one experiment at low temperatures. The vessel *A* was filled with clean broken ice, the opening into the stopcock being covered with fine gauze to prevent any small particles of ice from flowing out. The whole was then covered with cloth, to prevent melting. The vessel was then filled with water, and the two thermometers immersed to get the zero points. The calorimeter being about two thirds filled with water, and having been weighed, was then put in position, the holes corked up, and one thermometer placed in it, the other being in the melting ice. An observation of its temperature was then taken every minute, it being frequently stirred.

When enough observations had been obtained in this way, the cork was taken out of the aperture *F* and the spout inserted, and the water allowed to run for a given time, or until the calorimeter was full. It was then removed, the cork replaced, and the second thermometer removed from the ice to the calorimeter. Observations were then taken as before, and the vessel again weighed.

Two thermometers were used in the way specified, so that one might approach the final temperature from above and the other from below. But no regular difference was ever observed, and so some experiments were made with both thermometers in the calorimeter during the whole experiment.

The principal sources of error are as follows:—

1st. Thermometers lag behind their true reading. This was not noticed, and would probably be greater in thermometers with very fine stems like Geissler's. At any rate, it was almost eliminated in the experiment by using two thermometers.

2d. The water may be changed in temperature in passing through the spout. This was eliminated by allowing the water to run some time before it went into the calorimeter. The spout being very thin, and made of vulcanite, covered on the outside with cloth, it is not thought that there was any appreciable error. It will be discussed more at length below, and an experiment given to prove this.



3d. The top of the calorimeter not being in contact with the water, its temperature may be uncertain. To eliminate this, the calorimeter was often at the temperature of the air to commence with. Also the water was sometimes violently agitated just before taking the final reading, previous to letting in the cold water. Even if the temperature of this part was taken as that of the air, the error would scarcely ever be of sufficient importance to vitiate the conclusions.

4th. The specific heat of copper changes with the temperature. Unimportant.

5th. Some water might remain in the spout whose temperature might be different from the rest. This was guarded against.

6th. Evaporation. Impossible, as the calorimeter was closed.

7th. The introduction of cold water may cause dew to be deposited on the calorimeter. The experiments were rejected where this occurred.

The corrections for the protruding thermometer stem, for radiation, &c., were made as usual, the radiation being estimated by a series of observations before and after the experiment, as is usual in determining the specific heat of solids.

*June 14, 1878. — First Experiment.*

Time.	Ther. 6163.	Ther. 6166.	0 Points.	
41	296.75		6163, 57.9	Air, 21° C.
42	296.7		6165, 34.8	Jacket about 25° C.
43	296.7		6166, 20.5	
44	296.65			
<hr/>				
44½—44¾	Water running.		Calorimeter before	2043.0
46½	218.7	251.7	“ after	2853.8
47½	218.8	251.8	Water at 0° added	810.8
48½	218.9	252.0	Thermometer	1.1
			Total at 0°	811.4
<hr/>				
Temperature before	296.6		Calorimeter before	2043.0
Correction for 0	+ .2		Weight of vessel	388.8
	296.8 = 26°.597		Water	1654.7
Correction for stem	+ .019		Capacity of calorim.	35.4
Initial temp. of calorimeter	26°.616		“ thermom.	1.1
			Total capacity	1691.2

$218.6 + .2 = 218.8 = 17^{\circ}.994$	$251.6 - 1 = 251.5 = 17^{\circ}.962$
Correction for stem $-.006$	Correction for stem $-.006$
$17^{\circ}.988$	$17^{\circ}.956$

Mean temperature of mixture,  $17^{\circ}.972$ .

$$\frac{\text{Mean specific heat } 0 - 18^{\circ}}{\text{Mean specific heat } 18^{\circ} - 27^{\circ}} = \frac{1691.2 \times 8^{\circ}.644}{811.4 \times 17^{\circ}.972} = 1.0025.$$

*June 14. — Second Experiment.*

Calorimeter before 2016.3; temperature 361.4 by No. 6163.

“ after 3047.0; “ 244.5 and 288.7.

Air,  $21^{\circ}$  C.; jacket about  $27^{\circ}$ .

$361.4 + .2 = 361.6 = 33^{\circ}.803$ , or  $33^{\circ}.863$  when corrected for stem.

$244.5 + .2 = 244.7 = 20^{\circ}.865$ ; no correction for stem.

$288.7 - .1 = 288.6 = 20^{\circ}.846$ ; “ “

Mean,  $20^{\circ}.855$ .

$$\frac{\text{Mean specific heat between } 0 \text{ and } 21^{\circ}}{\text{Mean specific heat between } 21^{\circ} \text{ and } 34^{\circ}} = 1.0062.$$

*June 14. — Third Experiment.*

Calorimeter before 1961.8; temperature 293.6 by No. 6166.

“ after 3044.6; “ 243.7 and 213.0.

Air and jacket, about  $18^{\circ}$  C.

$393.6 - .1 = 393.5 = 29^{\circ}.036$ , or  $29^{\circ}.077$  when corrected for stem.

$243.7 - .1 = 243.6 = 17^{\circ}.849$ ; no correction for stem.

$213.0 + .2 = 213.2 = 17^{\circ}.874$ ; “ “

Mean,  $17^{\circ}.361$ .

$$\frac{\text{Mean specific heat between } 0 \text{ and } 17^{\circ}}{\text{Mean specific heat between } 17^{\circ} \text{ and } 29^{\circ}} = 1.0024.$$

It is to be observed that thermometer No. 6166 in all cases gave temperatures about  $0^{\circ}.02$  or  $0^{\circ}.03$  below No. 6163. This difference is undoubtedly in the determination of the zero points, as on June 15 the zero points were found to be 20.4 and 58.0. As one has gone up and the other down, the mean of the temperatures needs no correction.

*June 15.*

Calorimeter before 2068.2; temperature 364.6 by No. 6166.

" after 2929.2; " 249.7 and 217.7.

Air and jacket at about 22° C.

264.6 = 26°.766, or 26°.782 when corrected for stem.

249.7 = 17°.822, or 17°.812 " "

217.7 + .1 = 217.8 = 17°.884, or 17°.874 when corrected for stem.

Rejected on account of great difference in final temperatures by the two thermometers, which was probably due to some error in reading.

*June 21.*

Calorimeter before 2002.7; temperature 330.3 by No. 6163.

" after 3075.2; " 221.9 and 256.6.

Air and jacket, 21° C.

330.3 + .1 = 330.4 = 30°.321, or 30°.359 when corrected for stem.

221.9 + .1 = 222.0 = 18°.349, or 18°.343 " "

256.6 + .0 = 256.6 = 18°.358, or 18°.352 " "

Mean, 18°.347.

$$\frac{\text{Specific heat between } 0 \text{ and } 18^{\circ}}{\text{Specific heat between } 18^{\circ} \text{ and } 30^{\circ}} = 1.0067.$$

*June 21.*

Calorimeter before 2073.8; temperature 347.8 by No. 6166.

" after 2986.8; " 234.5 and 206.6.

Air and jacket, about 21° C.

347.8 + .0 = 347.8 = 25°.457, or 25°.471 when corrected for stem.

234.5 + .0 = 234.5 = 16°.643, or 16°.636 " "

206.6 + .1 = 206.7 = 16°.651, or 16°.644 " "

Mean, 16°.640.

$$\frac{\text{Specific heat between } 0 \text{ and } 17^{\circ}}{\text{Specific heat between } 17^{\circ} \text{ and } 25^{\circ}} = .99971.$$

Rejected because dew was formed on the calorimeter.

A series was now tried with both thermometers in the calorimeter from the beginning.

*June 25.*

Calor. before 2220.3; temperat. 325.6 by No. 6166; 309.9 by No. 6165.

" after 3031.4; " 233.4 " " 224.6 " "

Air, 24°.2 C.; jacket, 23°.5.

325.6 + .0 = 325.6 = 23°.725, or 23°.726 when corrected for stem.

309.9 + .2 = 310.1 = 23°.739, or 23°.740 " "

233.4 + .0 = 233.4 = 16°.558, or 16°.545 " "

224.6 + .2 = 224.8 = 16°.562, or 16°.549 " "

Means, 23°.733 and 16°.547.

$$\frac{\text{Specific heat between } 0 \text{ and } 16^\circ}{\text{Specific heat between } 16^\circ \text{ and } 24^\circ} = 1.0010.$$

*June 25.*

Calor. before 2278.6; temperat. 340.35 by No. 6166; 324.1 by No. 6165.

" after 3130.2; " 242.5 " " 232.8 " "

Air, 23°.5 C.; jacket, 22°.5.

340.35 + .0 = 340.35 = 24°.877, or 24°.881 when corrected for stem.

324.1 + .2 = 324.3 = 24°.899, or 24°.903 " "

242.5 + .0 = 242.5 = 17°.264, or 17°.253 " "

232.8 + .2 = 233.0 = 17°.261, or 17°.250 " "

$$\frac{\text{Specific heat between } 0 \text{ and } 17^\circ}{\text{Specific heat between } 17^\circ \text{ and } 25^\circ} = 1.0027.$$

*June 25.*

Calor. before 2316.35; temperat. 386.1 by No. 6166; 368.4 by No. 6165.

" after 2966.90; " 295.4 " " 281.7 " "

Air, 23°.5 C.; jacket, 22°.5.

386.1 + .0 = 386.1 = 28°.455, or 28°.465 when corrected for stem.

368.4 + .2 = 368.6 = 28°.472, or 28°.482 " "

295.4 + .0 = 295.4 = 21°.374, or 21°.368 " "

281.7 + .2 = 281.9 = 21°.400, or 21°.394 " "

Means, 28°.473 and 21°.381.

$$\frac{\text{Specific heat between } 0 \text{ and } 21^\circ}{\text{Specific heat between } 21^\circ \text{ and } 28^\circ} = 1.0045.$$

Two experiments were made on June 23 with warm water in vessel A, readings being taken of the temperature of the water, as it

flowed out, by one thermometer, which was then transferred to the calorimeter as before.

*June 23.*

Water in *A* while running, 314.15 by No. 6163.

Calor. before 1530.9; temperat. 281.1 by No. 6166.

" after 2996.3; " 328.4 by No. 6166; 272.7 by No. 6163.

$314.15 + .1 = 314.25 = 28^{\circ}.526$ , or  $28^{\circ}.552$  when corrected for stem.

$281.1 + .0 = 281.1 = 20^{\circ}.262$ , or  $20^{\circ}.258$  " "

$328.4 + .0 = 328.4 = 23^{\circ}.945$ , or  $23^{\circ}.950$  " "

$272.7 + .1 = 272.8 = 23^{\circ}.960$ , or  $23^{\circ}.966$  " "

$$\frac{\text{Specific heat between } 20^{\circ} \text{ and } 24^{\circ}}{\text{Specific heat between } 24^{\circ} \text{ and } 29^{\circ}} = .9983.$$

*June 23.*

Water in *A* while running, 883.9 by No. 6163.

Calor. before 1624.9; temperat. 286.75 by 6166.

" after 3048.2; " 892.45 by 6166, and 318.1 by 6163.

$883.9 + .1 = 884.0 = 36^{\circ}.303$ , or  $36^{\circ}.357$  when corrected for stem.

$286.75 + .0 = 286.75 = 20^{\circ}.702$ , or  $20^{\circ}.700$  " "

$892.45 + .0 = 892.45 = 28^{\circ}.954$ , or  $28^{\circ}.980$  " "

$318.1 + .1 = 318.2 = 28^{\circ}.964$ , or  $28^{\circ}.992$  " "

$$\frac{\text{Specific heat between } 21^{\circ} \text{ and } 29^{\circ}}{\text{Specific heat between } 29^{\circ} \text{ and } 36^{\circ}} = .9954.$$

To test the apparatus, and also to check the estimated specific heat of the calorimeter, the water was almost entirely poured out of the calorimeter, and warm water placed in the vessel *A*, which was then allowed to flow into the calorimeter.

Water in *A* while running, 309.0 by No. 6163.

Calor. before 391.3; temperat. 314.5 by 6166.

" after 3129.0; " 308.3 by 6166, and 878.5 by 6163.

Air about  $21^{\circ}$  C.

Therefore, water lost  $0^{\circ}.078$ , and calorimeter gained  $5^{\circ}$ . Hence the capacity of the calorimeter is 39.

Another experiment, more carefully made, in which the range was greater, gave 35.

The close agreement of these with the estimated amount is, of course, only accidental, for they depend upon an estimation of only  $0^{\circ}.08$  and  $0^{\circ}.12$  respectively. But they at least show that the water is delivered into the calorimeter without much change of temperature.

A few experiments were made as follows between ordinary temperatures and  $100^{\circ}$ , seeing that this has already been determined by Regnault.

Two thermometers were placed in the calorimeter, the temperature of which was about  $5^{\circ}$  below that of the atmosphere. The vessel B was then filled, and the water let into the calorimeter, by which the temperature was nearly brought to that of the atmosphere; the operation was then immediately repeated, by which the temperature rose about  $5^{\circ}$  above the atmosphere. The temperature of the boiling water was given by a thermometer whose  $100^{\circ}$  was taken several times.

As only the rise of temperature is needed, the zero points of the thermometers in the calorimeter are unnecessary, except to know that they are within  $0^{\circ}.02$  of correct.

*June 18.*

Temperature of boiling water,  $99^{\circ}.9$ .

Calor. before 2684.7; temperat. 259.2 by 6166, and 248.3 by 6165.

" after 2993.2; " 381.0 " " 363.4 "

259.3 =  $18^{\circ}.568$ , or  $18^{\circ}.555$  when corrected for stem.

248.3 =  $18^{\circ}.564$ , or  $18^{\circ}.551$  " "

381.0 =  $28^{\circ}.054$ , or  $28^{\circ}.065$  " "

363.4 =  $28^{\circ}.055$ , or  $28^{\circ}.066$  " "

$$\frac{\text{Specific heat } 28^{\circ} - 100^{\circ}}{\text{Specific heat } 18^{\circ} - 28^{\circ}} = 1.0024.$$

Other experiments gave 1.0015 and 1.0060, the mean of all of which is 1.0033. Regnault's formula gives 1.005; but going directly to his experiments, we get about 1.004, the other quantity being for  $110^{\circ}$ .

The agreement is very satisfactory, though one would expect my small apparatus to lose more of the heat of the boiling water than Regnault's. Indeed, for high temperatures my apparatus is much inferior to Regnault's, and so I have not attempted any further experiments at high temperatures.

My only object was to confirm by this method the results deduced from the experiments on the mechanical equivalent; and this I have done, for the experiments nearly all show that the specific heat of water *decreases* to about  $30^{\circ}$ , after which it increases. But the mechanical equivalent experiments give by far the most accurate solution of the problem; and, indeed, give it with an accuracy hitherto unattempted in experiments of this nature.

But whether water increases or decreases in specific heat from  $0^{\circ}$  to  $30^{\circ}$  depends upon the determination of the reduction to the air thermometer. *According to the mercurial thermometers Nos. 6163, 6165, and 6166, treating them only as mercurial thermometers, the specific heat of water up to  $30^{\circ}$  is nearly constant, but by the air thermometer, or by the Kew standard or Fastré, it decreases.*

Full and complete tables of comparison are published, and from them any one can satisfy himself of the facts in the case.

I am myself satisfied that I have obtained a very near approximation to absolute temperatures, and accept them as the standard. And by this standard the specific heat of water undoubtedly decreases from  $0^{\circ}$  to about  $30^{\circ}$ .

To show that I have not arrived at this result rashly, I may mention that I fought against a conclusion so much at variance with my preconceived notions, but was forced at last to accept it, after studying it for more than a year, and making frequent comparisons of thermometers, and examinations of all other sources of error.

However remarkable this fact may be, being the first instance of the decrease of the specific heat with rise of temperature, it is no more remarkable than the contraction of water to  $4^{\circ}$ . Indeed, in both cases the water hardly seems to have recovered from freezing. The specific heat of melting ice is infinite. Why is it necessary that the specific heat should instantly fall, and then recover as the temperature rises? Is it not more natural to suppose that it continues to fall even after the ice is melted, and then to rise again as the specific heat approaches infinity at the boiling point? And of all the bodies which we should select as probably exhibiting this property, water is certainly the first.

#### (b.) Heat Capacity of Calorimeter.

During the construction of the calorimeter, pieces of all the material were saved in order to obtain the specific heat. The calorimeter which Joule used was put together with screws, and with little or no solder. But in my calorimeter it was necessary to use solder, as it was of a

much more complicated pattern. The total capacity of the solder used was only about  $\frac{1}{800}$  of the total capacity including the water; and if we should neglect the whole, and call it copper, the error would be only about  $\frac{1}{1200}$ . Hence it was considered sufficient to weigh the solder before and after use, being careful to weigh the scraps. The error in the weight of solder could not possibly have been as great as ten per cent., which would affect the capacity only 1 part in 12,000.

To determine the nickel used in plating, the calorimeter was weighed before and after plating; but it weighed less after than before, owing to the polishing of the copper. But I estimated the amount from the thickness of a loose portion of the plating. I thus found the approximate weight of nickel, but as it was so small, I counted it as copper. The following are the constituents of the calorimeter:—

Thick sheet copper . . . . .	25.1	per cent.
Thin " " " . . . . .	45.7	"
Cast brass . . . . .	17.9	"
Rolled or drawn brass . . . . .	5.7	"
Solder . . . . .	4.0	"
Steel . . . . .	1.6	"
	<hr/> 100.0	"
Nickel . . . . .	.3	"

To determine the mean specific heat, the basket of a Regnault's apparatus was filled with the scraps in the above proportion, allowing the basket of brass gauze, which was very light, to count toward the drawn brass. The specific heat was then determined between 20° and 100°, and between about 10° and 40°. Between 20° and 100° the ordinary steam apparatus was used, but between 10° and 40° a special apparatus filled with water was used, the water being around the tube containing the basket, in the same manner as the steam is in the original apparatus. In the calorimeter a stirrer was used, so that the basket and water should rapidly attain the same temperature. The water was weighed before and after the experiment, to allow for evaporation. A correction of about 1 part in 1,000 was made, on account of the heat lost by the basket in passing from the apparatus to the calorimeter, in the 100° series, but no correction was made in the other series. The thermometers in the calorimeter were Nos. 6163 and 6166 in the different experiments.

The principal difficulty in the determination is in the correction for radiation, and for the heat which still remains in the basket after some



time. After the basket has descended into the water, it commences to give out heat to the water; this, in turn, radiates heat; and the temperature we measure is dependent upon both these quantities.

Let  $T$  = temperature of the basket at the time  $t$

"  $T'$  = " " " " 0

"  $T''$  = " " " "  $\infty$

"  $\theta$  = " " water "  $t$

"  $\theta'$  = " " " " 0

"  $\theta''$  = " " " "  $\infty$

$$\theta'' = T''$$

We may then put approximately

$$T - T'' = (T' - T'') s^{-\frac{t}{c}},$$

where  $c$  is a constant. But

$$\frac{T' - T''}{\theta'' - \theta'} = \frac{T' - T}{\theta - \theta'};$$

hence

$$\theta - \theta' = (\theta'' - \theta') (1 - s^{-\frac{t}{c}}).$$

To find  $c$  we have

$$c = \frac{1}{t} \log_s \frac{\theta'' - \theta'}{\theta - \theta'},$$

where  $\theta''$  can be estimated sufficiently accurately to find  $C'$  approximately.

These formulæ apply when there is no radiation. When radiation takes place, we may write, therefore, when  $t$  is not too small,

$$\theta - \theta' = (\theta'' - \theta') (1 - s^{-\frac{t}{c}}) - C (t - t_0),$$

where  $C$  is a coefficient of radiation, and  $t_0$  is a quantity which must be subtracted from  $t$ , as the temperature of the calorimeter does not rise instantaneously. To estimate  $t_0$ ,  $T_a$  being the temperature of the air, we have, according to Newton's law of cooling,

$$C (t - t_0) = \frac{C}{\theta'' - T_a} \int_0^t (\theta - T_a) dt \text{ nearly,}$$

$$t_0 = c \frac{\theta'' - \theta'}{\theta'' - T_a} \text{ nearly,}$$

where it is to be noted that  $\frac{C}{\theta'' - T_a}$  is nearly a constant for all values of  $\theta'' - T_a$  according to Newton's law of cooling.

The temperature reaches a maximum nearly at the time

$$t_m = c \log_e \frac{\theta'' - \theta'}{c C};$$

and if  $\theta_m$  is the maximum temperature, we have the value of  $\theta''$  as follows:

$$\theta'' = T'' = \theta_m + C(t_m + c - t_0);$$

$$T'' = \theta_m + C\left(t_m + c \frac{T_a - \theta'}{\theta'' - T_a}\right);$$

and this is the final temperature provided there was no loss of heat.

When the final temperature of the water is nearly equal to that of the air,  $C$  will be small, but the time  $t_m$  of reaching the maximum will be great. If  $a$  is a constant, we can put  $C = a(\theta'' - T_a)$ , and  $C(t_m + c - t_0)$  will be a minimum, when

$$C = \frac{\theta'' - \theta'}{c}, \quad \text{or} \quad T_a = \theta'' - \frac{\theta'' - \theta'}{ac}.$$

That is, the temperature of the air must be lower than the temperature of the water, so that  $T_a = \theta''$  as nearly as possible; but the formula shows that this method makes the corrections greater than if we make  $T_a = \theta'$ , the reason being that the maximum temperature is not reached until after an infinite time. It will in practice, however, be found best to make the temperature of the water at the beginning about that of the air. It is by far the best and easiest method to make all the corrections graphically, and I have constructed the following graphical method from the formulæ.

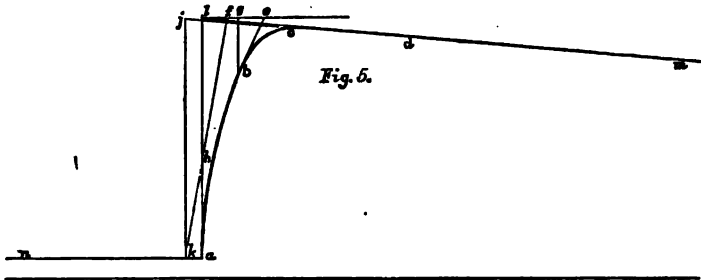
First make a series of measurements of the temperature of the water of the calorimeter, before and after the basket is dipped, together with the times. Then plot them on a piece of paper as in Fig. 5, making the scale sufficiently large to insure accuracy. Five or ten centimeters to a degree are sufficient.

$nabcd$  is the plot of the temperature of the water of the calorimeter, the time being indicated by the horizontal line. Continue the line  $dc$  until it meets the line  $la$ . Draw a horizontal line through the point  $l$ . At any point,  $b$ , of the curve, draw a tangent and also a vertical line  $bg$ ; the distance  $eg$  will be nearly the value of the constant  $c$  in the formulæ. Lay off  $lf$  equal to  $c$ , and draw the line  $fhk$  through the point  $h$ , which indicates the temperature of the atmosphere or of the vessel surrounding the calorimeter. Draw a vertical line,  $jk$ , through the point  $k$ . From the point of maximum,

$a$ , draw a line,  $jc$ , parallel to  $dm$ , and where it meets  $kj$  will be the required point, and will give the value of  $\theta''$ . Hence, the rise of temperature, corrected for all errors, will be  $kj$ .

This method, of course, only applies to cases where the final temperature of the calorimeter is greater than that of the air; otherwise there will be no maximum.

In practice, the line  $dm$  is not straight, but becomes more and more nearly parallel to the base line. This is partly due to the constant decrease of the difference of temperature between the calorimeter and the air, but is too great for that to account for it. I have traced it to the thin metal jacket surrounding the calorimeter, and I must condemn, in the strongest possible manner, all such arrangements of calorimeters as have such a thin metal jacket around them. The jacket is



of an uncertain temperature, between that of the calorimeter and the air. When the calorimeter changes in temperature, the jacket follows it, but only after some time; hence, the heat lost in radiation is uncertain. The true method is to have a water jacket of constant temperature, and then the rate of decrease of temperature will be nearly constant for a long time.

The following results have been obtained by Mr. Jacques, Fellow of the University, though the first was obtained by myself. Corrections were, of course, made for the amount of thermometer stem in the air.

Temperature.	Mean Specific Heat.
24° to 100°	.0915
26° " 100°	.0915
25° " 100°	.0896
13° " 39°	.0895
14° " 38°	.0885
9° " 41°	.0910

To reduce these to the mean temperature of  $0^{\circ}$  to  $40^{\circ}$ , I have used the rate of increase found by Bède for copper. They then become, for the mean from  $0^{\circ}$  to  $40^{\circ}$ , —

.0897
.0897
.0878
.0893
.0883
.0906
Mean .0892 $\pm$ .00027

As the capacity of the calorimeter is about four per cent of that of the total capacity, including the water, this probable error is about  $\frac{1}{250}$  of the total capacity, and may thus be considered as satisfactory.

I have also computed the mean specific heat as follows, from other observers : —

Copper between  $20^{\circ}$  and  $100^{\circ}$  nearly.

.0949	Dulong.
.0935	} Regnault.
.0952	
.0933	Bède.
.0930	Kopp.
.0940	

This reduced to between  $0^{\circ}$  and  $40^{\circ}$  by Bède's formula gives .0922. Hence we have the following for the calorimeter : \* —

	Per cent.	Specific Heat between $0^{\circ}$ and $40^{\circ}$ C.
Copper	91.4	.0922
Zinc	.7	.0896
Tin	3.6	.0550
Lead	2.7	.0310
Steel	1.6	.1110
		Mean .0895

The close agreement of this number with the experimental result can only be accidental, as the reduction to the air thermometer would decrease it somewhat, and so make it even lower than mine. How-

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\* The cast brass was composed of 28 parts of copper, 2 of tin, 1 of zinc, and 1 of lead. The rolled brass was assumed to have the same composition. The solder was assumed to be made of equal parts of tin and lead.

ever, the difference could not at most amount to more than 0.5 per cent, which is very satisfactory.

The total capacity of the calorimeter is reckoned as follows:—

Weight of calorimeter	3.8712	kilogrammes.
“ screws	.0016	“
“ part of suspending wires	.0052	“
Total weight	3.8780	“

$$\text{Capacity} = 3.878 \times .0892 = .3459 \text{ kilogrammes.}$$

To this must be added the capacity of the thermometer bulb and several inches of the stem, and of a tube used as a safety valve, and we must subtract the capacity of a part of the shaft which was joined to the shaft turning the paddles. Hence,

$$\begin{array}{r} .3459 \\ + .0011 \\ + .0010 \\ - .0010 \\ \hline \text{Capacity} = .3470 \end{array}$$

As this is only about four per cent of the total capacity, it is not necessary to consider the variation of this quantity with the temperature through the range from 0° to 40° which I have used.

#### IV. DETERMINATION OF EQUIVALENT.

##### (a.) Historical Remarks.

The history of the determination of the mechanical equivalent of heat is that of thermodynamics, and as such it is impossible to give it at length here.

I shall simply refer to the few experiments which *a priori* seem to possess the greatest value, and which have been made rather for the determination of the quantity than for the illustration of a method, and shall criticise them to the best of my ability, to find, if possible, the cause of the great discrepancies.

##### 1. GENERAL REVIEW OF METHODS.

Whenever heat and mechanical energy are converted the one into the other, we are able by measuring the amounts of each to obtain the ratio. Every equation of thermodynamics proper is an equation

between mechanical energy and heat, and so should be able to give us the mechanical equivalent. Besides this, we are able to measure a certain amount of electrical energy in both mechanical and heat units, and thus to also get the ratio. Chemical energy can be measured in heat units, and can also be made to produce an electric current of known mechanical energy. Indeed, we may sum up as follows the different kinds of energy whose conversion into one another may furnish us with the mechanical equivalent of heat. And the problem in general would be the ratio by which each kind of energy may be converted into each of the others, or into mechanical or absolute units.

- a. Mechanical energy.
- b. Heat.
- c. Electrical energy.
- d. Magnetic “
- e. Gravitation “
- f. Radiant “
- g. Chemical “
- h. Capillary “

Of these different kinds of energy, only the first five can be measured other than by their conversion into other forms of energy, although Sir William Thomson, by the introduction of such terms as “cubic mile of sunlight,” has made some progress in the case of radiation. Hence for these five only can the ratio be known.

Mechanical energy is measured by the force multiplied by the distance through which the force acts, and also by the mass of a body multiplied by half the square of its velocity. Heat is usually referred to the quantity required to raise a certain amount of water so many degrees, though hitherto the temperature of the water and the reduction to the air thermometer have been almost neglected.

The energy of electricity at rest is the quantity multiplied by half the potential; or of a current, it is the strength of current multiplied by the electro-motive force, and by the time; or for all attractive forces varying inversely as the square of the distance, Sir William Thomson has given the expression

$$\frac{1}{8\pi} \int R^2 dv,$$

where  $R$  is the resultant force at any point in space, and the integral is taken throughout space.

These last three kinds of energy are already measured in absolute

measure, and hence their ratios are accurately known. The only ratio, then, that remains is that of heat to one of the others, and this must be determined by experiment alone.

But although we cannot measure  $f$ ,  $g$ ,  $h$  in general, yet we can often measure off equal amounts of energy of these kinds. Thus, although we cannot predict what quantities of heat are produced when two atoms of different substances unite, yet, when the same quantities of the same substances unite to produce the same compound, we are safe in assuming that the same quantity of chemical energy comes into play.

According to these principles, I have divided the methods into direct and indirect.

Direct methods are those where  $b$  is converted directly or indirectly into  $a$ ,  $c$ ,  $d$ , or  $e$ , or *vice versa*.

Indirect methods are those where some kind of energy, as  $g$ , is converted into  $b$ , and also into  $a$ ,  $c$ ,  $d$ , or  $e$ .

In this classification I have made the arrangement with respect to the kinds of energy which are measured, and not to the intermediate steps. Thus Joule's method with the magneto-electric machine would be classed as mechanical energy into heat, although it is first converted into electrical energy. The table does not pretend to be complete, but gives, as it were, a bird's-eye view of the subject. It could be extended by including more complicated transformations; and, indeed, the symmetrical form in which it is placed suggests many other transformations. As it stands, however, it includes all methods so far used, besides many more.

In the table of indirect methods, the kind of energy mentioned first is to be eliminated from the result by measuring it both in terms of heat and one of the other kinds of energy, whose value is known in absolute or mechanical units.

It is to be noted that, although it is theoretically possible to measure magnetic energy in absolute units, yet it cannot be done practically with any great accuracy, and is thus useless in the determination of the equivalent. It could be thus left out from the direct methods without harm, as also out of the next to last term in the indirect methods.

TABLE XXV.—SYNOPSIS OF METHODS FOR OBTAINING THE MECHANICAL EQUIVALENT OF HEAT.

A. Direct.	α. Heat { Mechanical Energy Gravitation "	1. Reversible Process	<ul style="list-style-type: none"> <li>a. Expansion or compression according to adiabatic curve.</li> <li>b. Expansion or compression according to isothermal curve.</li> <li>c. Expansion or compression according to any curve with regenerator.</li> <li>d. Electro-magnetic engine driven by thermo-electric pile in a circuit of no resistance.</li> </ul>
		2. Irreversible Process	<ul style="list-style-type: none"> <li>a. Friction, percussion, etc.</li> <li>b. Heat from magneto-electric currents, or electric machine.</li> </ul>
	β. Heat, Electric Energy . .	1. Reversible Process	<ul style="list-style-type: none"> <li>a. Thermo-electric currents</li> <li>b. Pyro-electric phenomena (probably).</li> </ul>
		2. Irreversible Process	<ul style="list-style-type: none"> <li>a. Heating of wire by current, or heat produced by discharge of electric battery.</li> </ul>
	γ. Heat, Magnetic Energy . .	1. Reversible Process	<ul style="list-style-type: none"> <li>a. Thermo-electric current magnetizing a magnet in a circuit of no resistance.</li> </ul>
		2. Irreversible Process	<ul style="list-style-type: none"> <li>a. Heating of magnet when demagnetized.</li> </ul>
B. Indirect.	α. Radiant Energy, Heat . . (Irradiant energy absorbed by blackened surface.)	a. Mechanical Energy.	Crooke's radiometer.
		b. Electrical "	Thermo-electric pile.
		c. Magnetic "	Thermo-electric pile with electro-magnet in circuit.
		d. Gravitation "	
	β. Chemical Energy, Heat . . (Combustion, etc.)	a. Mechanical Energy	<ul style="list-style-type: none"> <li>1. Cannon.</li> <li>2. Electro-magnetic machine run by galv. battery.</li> </ul>
		b. Electrical "	Current from battery.
		c. Magnetic "	Electro-magnet magnetized by a battery current.
		d. Gravitation "	
	γ. Capillary energy, Heat . . (Heat produced when a liquid is absorbed by a porous solid.)	a. Mechanical Energy.	Movement of liquid by capillarity.
		b. Electrical "	Electrical currents from capillary action at surface of mercury.
		c. Magnetic "	
		d. Gravitation "	Raising of liquid by capillarity.
	δ. Electrical energy, Heat . . (Heat generated in a wire by an electrical current.)	a. Mechanical Energy	Magneto-electric or electro-magnetic machine. Electric attraction.
		b. Magnetic "	Electro-magnet.
		c. Gravitation "	
	ε. Magnetic Energy, Heat . . (Heat generated on demagnetizing a magnet.)	a. Mechanical Energy	Armature attracted by a permanent magnet.
		b. Electrical "	Induced current on demagnetizing a magnet.
		c. Gravitation "	
	ζ. Gravitation Energy, Heat . . (Heat generated by a falling body.)	a. Mechanical Energy.	Velocity imparted to a falling body.
		b. Electrical "	
		c. Magnetic "	

## 2. RESULTS OF BEST DETERMINATIONS.

On the basis of this table of methods I have arranged the following table, showing the principal results so far obtained.

In giving the indirect results, many persons have only measured one of the transformations required; and as it would lengthen out the





table very much to give the complete calculation of the equivalent from these selected two by two, I have sometimes given tables of these parts. As the labor of looking up and reducing these is very great, it is very possible that there have been some omissions.

I have taken the table published by the Physical Society of Berlin,<sup>1</sup> as the basis down to 1857, though many changes have been made even within this limit.

I shall now take up some of the principal methods, and discuss them somewhat in detail.

*Method from Theory of Gases.*

As the different constants used in this method have been obtained by many observers, I shall first give their results.

TABLE XXVII.—SPECIFIC HEAT OF GASES.

	Limit to Temperature.	Approximate Temperature of Water.	Temperature reduced to	Specific Heat.	
Air. . . . .	.....	.....	{ Mercurial Thermometer }	.2669	{ Delaroche and Bérard.
	20° to 210°	*14°.2	{ Air Thermometer }	.23751 <sup>16</sup>	{ Regnault.
	20° to 100°	20°	{ Mercurial Thermometer }	.2389 <sup>17</sup>	{ E. Wiedemann.
Hydrogen . . . . .	.....	.....	{ Mercurial Thermometer }	3.2986	{ Delaroche and Bérard.
	15° to 200°	12°.2	{ Air Thermometer }	3.4090 <sup>16</sup>	{ Regnault.
	21° to 100°	21°	{ Mercurial Thermometer }	3.410 <sup>17</sup>	{ E. Wiedemann.

TABLE XXVIII.—COEFFICIENT OF EXPANSION OF AIR UNDER CONSTANT VOLUME.

	Taking Expansion of Mercury according to Regnault.	Taking Expansion of Mercury according to Willner's Recalculation of Regnault's Experiments.
Regnault . . . . .	.0036655	.0036687
Magnus . . . . .	.0036678	.0036710
Jolly . . . . .	.0036695	.0036727
Rowland . . . . .	.0036675	.0036707
Mean . . . . .	.0036676	.0036708

\* Taking mean of results on page 101 of *Rel. des Exp.*, tom. ii.

TABLE XXIX.—RATIO OF SPECIFIC HEATS OF AIR.

Method.	Observer.	Date.	Ratio of specific heats.
Method of Clément & Désormes, globe 20 litres . . }	Clément & Désormes <sup>18</sup> }	1812	} 1.854
Never fully published . . . . .	Gay-Lussac & Welter <sup>19</sup> . . . . .	Published in 1819	
Method of Clément & Désormes . . . . .	Delaroche & Bérard <sup>41</sup> . . . . .	1819	1.3748
Using Breguet thermometer . . . . .	Favre & Silbermann <sup>28</sup> . . . . .	1853	1.249
Clément & Désormes, globe 89 litres . . . . .	Masson <sup>29</sup> . . . . .	1858	1.421
Clément & Désormes . . . . .	Weisbach <sup>21</sup> . . . . .	1859	1.4196
Clément & Désormes, globe 10 litres . . . . .	Hirn <sup>22</sup> . . . . .	1861	1.4025
Passage of gas from one vessel into another, globes 60 litres . . . . .	Cazin <sup>24</sup> . . . . .	1862	1.3845
Pressure in globe changed by aspirator, globe 25 litres . . . . .	Dupré <sup>23</sup> . . . . .	1863	1.41
Heating of gas by electric current . . . . .	Jamin & Richard <sup>28</sup> . . . . .	1864	1.41
Clément & Désormes . . . . .	Tresca et Laboulaye <sup>22</sup> . . . . .	1864	1.302
Barometer under air-pump receiver of 6 litres . . . . .	Kohlrausch <sup>23</sup> . . . . .	1869	} Results lost in the siege of Paris.
Compression and expansion of gas by piston . . . . .	Regnault . . . . .	1871	
Clément & Désormes with metallic manometer, globe 70 litres . . . . .	Röntgen <sup>27</sup> . . . . .	1878	
Compression of gas by piston . . . . .	Amagat <sup>30</sup> . . . . .	1874	1.4053
			1.307

## References. (Tables XXVI. to XXX.)

- <sup>1</sup> Physical Society of Berlin, Fort. der Phys., 1858.
- <sup>2</sup> Joule, Phil. Mag., ser. 3, vol. xxvi. See also Mec. Wärmeäquivalent, Gesammelte Abhandlungen von J. P. Joule, Braunschweig, 1872.
- <sup>3</sup> Joule, Phil. Mag., ser. 3, vol. xxiii. See also 2 above.
- <sup>4</sup> " " " " " xxvi. " "
- <sup>5</sup> " " " " " xxvii. " "
- <sup>6</sup> " " " " " xxxi. " "
- <sup>7</sup> Hirn, Théorie Méc. de la Chaleur, ser. 1, 3<sup>me</sup> ed.
- <sup>8</sup> Edlund, Pogg. Ann., cxiv. 1, 1865.
- <sup>9</sup> Favre, Comptes Rend., Feb. 15, 1858; also Phil. Mag., xv. 406.
- <sup>10</sup> Violle, Ann. de Chim., ser. 4, xxii. 64.
- <sup>11</sup> Quintus Icilius, Pogg. Ann., ci. 69.
- <sup>12</sup> Boscha, Pogg. Ann., cviii. 162.
- <sup>13</sup> Joule, Report of the Committee on Electrical Standards of the B. A., London, 1873, p. 175.
- <sup>14</sup> H. F. Weber, Phil. Mag., ser. 5, v. 30.
- <sup>15</sup> Favre, Comptes Rend., xlvii. 699.
- <sup>16</sup> Regnault, Rel. des Expériences, tom. ii.
- <sup>17</sup> E. Wiedemann, Pogg. Ann., clvii. 1.

TABLE XXX.—PRINCIPAL VALUES OF THE VELOCITY OF SOUND.

Number.	Observer.	Date.	Place.	Number of Observations.	Temperature Observed.	Velocity Observed.	Velocity reduced to 0° and Ordinary Air.	Velocity reduced to 0° and Dry Air.	Velocity approximately reduced to 0° and Dry Air.
1	French Academy <sup>§1</sup>	1788	France	....	6° to 7° 5 C.	172.56 T.	332.9 m.	....	332.6
2	Benzenberg <sup>§2</sup>	1811	Dusseldorf	40	.....	....	*333.7 m.	....	332.7
3	Goldingham <sup>§3</sup>	1821	India	120	83° 95 F.	1149.2 ft.	†338.0 cm.	....	332.6
4	"	1821	India	70	79° 9 F.	1131.5 ft.	†329.36 m.	....	328.1
5	Bureau of Longitude <sup>§4</sup>	1822	France	80	16° 9 C.	340.89 m.	331.36 m.	....	330.8
6	Stampfer & Von Myrbach <sup>§5</sup>	1822	Austria	88	9° 4 C.	....	332.96 m.	....	332.5
7	Moll & Van Beek <sup>§6</sup>	1823	Holland	22 shots	11° 16 C.	840.37	333.62	\$332.82	....
8	"	1823	Holland	14 shots	†11° 00 C.	339.27	332.62	\$331.91	....
9	Parry & Foster <sup>§7</sup>	1824-5	Port Bowen	51	-38° F. to +38° F.	....	332.27	....	332.0
10	Savart <sup>§8</sup>	1839	.....	....	5° 5 to 9° C.	330.5	†332.2	....	331.8
11	Brown & Martins <sup>§9</sup>	1844	Alps	24	8° 17 C.	338.01	333.11	332.37	....
12	Regnault <sup>§10</sup>	1864	France	149	2° to 20° C.	....	....	330.71	....

<sup>§1</sup> Reduced to 0° by empirical formula.  
<sup>§2</sup> Moll & Van Beek found 332.049 m. at 0° in dry air. They used the coefficient .00375 to reduce. I take the numbers as recalculated by Schröder van der Kolk.  
<sup>§3</sup> Corrected for wind by Galbraith.  
<sup>§4</sup> See I believe that I calculated these reduced numbers on the supposition that the air was rather more than half saturated with moisture.  
<sup>§5</sup> Wind calm.  
<sup>§6</sup> An error of 0° 21 C. was made in the original. See Schröder van der Kolk, Phil. Mag., 1866.  
<sup>§7</sup> I take the numbers as recalculated by Schröder van der Kolk.  
<sup>§8</sup> Recalculated from Savart's results.  
<sup>§9</sup> Recalculated from Savart's results.  
<sup>§10</sup> Recalculated from Savart's results.

Estimating the weight rather arbitrarily, I have combined them as follows:—

No.	Velocity at 0°. C. Dry Air.	Estimated Weight of Observation.
1	332.6	2
2	332.7	2
3	330.9	2
4	330.8	4
5	332.5	3
6	332.8	7
7	332.0	1
8	331.8	1
9	332.4	4
10	330.7	10
Mean	331.75	

Or, corrected for the normal carbonic acid in the atmosphere, it becomes 331.78 meters per second in dry pure air at 0° C.

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- <sup>18</sup> Clément et Désormes, *Journal de Physique*, lxxxix. 333, 1810.  
<sup>19</sup> Laplace, *Méc. Céleste*, v. 125.  
<sup>20</sup> Masson, *Ann. de Chim. et de Phys.*, ser. 3, tom. liii.  
<sup>21</sup> Weisbach, *Der Civilingenieur*, Neue Folge, Bd. v., 1859.  
<sup>22</sup> Hirn, *Théorie Méc. de la Chaleur*, i. 111.  
<sup>23</sup> Favre et Silbermann, *Ann. de Chim.*, ser. 3, xxxvii. 1851.  
<sup>24</sup> Cazin, *Ann. de Chim.*, ser. 3, tom. lxvi.  
<sup>25</sup> Dupré, *Ann. de Chim.*, 8<sup>me</sup> ser., lxvii. 359, 1863.  
<sup>26</sup> Kohlrausch, *Pogg. Ann.*, cxxxvi. 618.  
<sup>27</sup> Röntgen, *Pogg. Ann.*, cxlviii. 608.  
<sup>28</sup> Jamin and Richard, *Comptes Rend.*, lxxi. 336.  
<sup>29</sup> Tresca and Laboulaye, *Comptes Rend.*, lviii. 358. *Ann. du Conserv. des Arts et Métiers*, vi. 365.  
<sup>30</sup> Amagat, *Comptes Rend.*, lxxvii. 1825.  
<sup>31</sup> *Mém. de l'Acad. des Sci.*, 1788, p. 128.  
<sup>32</sup> Benzenberg, *Gilbert's Annalen*, xlii. 1.  
<sup>33</sup> Goldingham, *Phil. Trans.*, 1823, p. 96.  
<sup>34</sup> *Ann. de Chim.*, 1822, xx. 210; also, *Œuvres de Arago*, *Mém. Sci.*, ii. 1.  
<sup>35</sup> Stampfer and Von Myrbach, *Pogg. Ann.*, v. 406.  
<sup>36</sup> Moll and Van Beek, *Phil. Trans.*, 1824, p. 424. See also Shröder van der Kolk, *Phil. Mag.*, 1865.  
<sup>37</sup> Parry and Foster, *Journal of the Third Voyage*, 1824–5, Appendix, p. 86. *Phil. Trans.*, 1828, p. 97.  
<sup>38</sup> Savart, *Ann. de Chim.*, ser. 2, lxxi. 20. Recalculated.  
<sup>39</sup> Bravais and Martins, *Ann. de Chim.*, ser. 3, xiii. 5.  
<sup>40</sup> Regnault, *Rel. des Exp.*, iii. 538.  
<sup>41</sup> Delaroche and Bérard, *Ann. de Chim.*, lxxxv. 72 and 118.  
<sup>42</sup> Puluj, *Pogg. Ann.*, clvii. 656.

From Regnault's experiments on the velocity in pipes I find by graphical means 331.4<sup>m</sup> in free air, which is very similar to the above.

*Calculation from Properties of Gases.*

$K$  = specific heat of gas at constant pressure.

$k$  = " " " " volume.

$p$  = pressure in absolute units of a unit of mass.

$v$  = volume " " " "

$\mu$  = absolute temperature.

$J$  = Joule's equivalent in absolute measure.

$$\gamma = \frac{K}{k}.$$

General formula for all bodies :—

$$\gamma = \frac{1}{1 - \frac{\mu}{JK} \left( \frac{dp}{d\mu} \right)_v \left( \frac{dv}{d\mu} \right)_p},$$

$$\gamma = - \frac{V^2}{v^2} \left( \frac{dv}{dp} \right)_\mu;$$

$$\therefore J = \frac{\mu}{K} \left( \frac{dp}{d\mu} \right)_v \left( \frac{dv}{d\mu} \right)_p \frac{\gamma}{\gamma-1}.$$

Also,

$$J = - \frac{\mu}{K} \frac{\left( \frac{dr}{d\mu} \right)_p^2}{\left( \frac{dv}{dp} \right)_\mu + \frac{v^2}{V^2}}.$$

Application to gases; Rankine's formula is,—

$$pv = R \left( \mu - m \frac{\mu_0}{\mu} \frac{v_0}{v} \right),$$

$$\left( \frac{dp}{d\mu} \right)_v = \frac{p}{\mu} \left( 1 + 2 m \frac{\mu_0}{\mu} \frac{v_0}{v} \right),$$

$$\left( \frac{dv}{d\mu} \right)_p = \frac{v}{\mu} \left( 1 + 3 m \frac{\mu_0}{\mu} \frac{v_0}{v} \right),$$

$$\left( \frac{dv}{d\mu} \right)_\mu = - R \frac{\mu}{p^2} = - \frac{p_0 v_0}{\mu_0} \frac{\mu}{p^2} \left( 1 + \frac{m}{\mu_0} \right).$$

If  $\alpha_v$  is the coefficient of expansion between 0° and 100°, then

$$\mu_0 = \frac{1}{\alpha_v} (1 + .00633 m);$$

whence

$$J = \frac{p v \mu}{K} \alpha'_p \alpha'_v \left( \frac{\gamma}{\gamma-1} \right),$$

where  $\alpha'_p$  and  $\alpha'_v$  are the true coefficients of expansion at the given temperature ;

$$\therefore J = \frac{p v}{K \mu} \left( 1 + 6 m \frac{\mu_o}{\mu^2} \frac{r_o}{v} \right) \frac{\gamma}{\gamma - 1} ;$$

$$J = \frac{1}{K \mu} \frac{1 + 6 m \frac{\mu_o}{\mu^2} \frac{r_o}{v}}{\frac{\mu_o v_o \mu}{p^2 v^2 \mu_o} \left( 1 + \frac{m}{\mu_o} \right) - \frac{1}{V^2} \left( \frac{r_o}{v} \right)^2}.$$

According to Thomson and Joule's experiments  $m = 0^\circ.83$  C. for air and about  $2^\circ.0$  for  $\text{CO}_2$ . Hence  $\mu_o = 272^\circ.99$ .

The equations should be applied to the observations directly at the given temperature, but it will generally be sufficient to use them after reduction to  $0^\circ$  C. Using  $K = .2375$  according to Regnault for air, we have for the latitude of Baltimore, —

From Röntgen's value $\gamma = 1.4053$	$\frac{J}{g} = 430.3^*.$
" Amagat's " 1.397	$\frac{J}{g} = 436.6.$
" velocity of sound 331.78 <sup>m</sup> per sec.	$\frac{J}{g} = 429.6.$

Using Wiedemann's value for  $K$ , .2389, these become

$$\frac{J}{g} = 427.8; \quad \frac{J}{g} = 434.0; \quad \frac{J}{g} = 427.1.$$

As Wiedemann, however, used the mercurial thermometer, and as the reduction to the air thermometer would increase these figures from .2 to .8 per cent., it is evident that Regnault's value for  $K$  is the more nearly correct. I take the weights rather arbitrarily as follows : —

	Weight.	$\frac{J}{g}$
Röntgen	3	430.3
Amagat	1	436.6
Velocity of sound	4	429.6
		Mean 430.7

And this is of course the value referred to water at  $14^\circ$  C. and in the latitude of Baltimore. My value at this point is 427.7.

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\* Röntgen gives the value 428.1 for the latitude of Paris as calculated by a formula of Shröder v. d. Kolk, and 427.8 from the formula for a perfect gas, and these both agree more nearly with my result than that calculated from my own formula.

This determination of the mechanical equivalent from the properties of air is at most very imperfect, as a very slight change in either  $\gamma$  or the velocity of sound will produce a great change in the mechanical equivalent.

*From Theory of Vapors.*

Another important method of calculating the mechanical equivalent of heat is from the equation for a body at its change of state, as for instance in vaporization. Let  $v$  be the volume of the vapor, and  $v'$  the volume of the liquid, and  $H$  the heat required to vaporize a unit of mass of the water; also let  $p$  be the pressure in absolute units, and  $\mu$  the absolute temperature. Then

$$v - v' = \frac{JH}{\mu \left( \frac{dp}{d\mu} \right)}.$$

The quantity  $H$  and the relation of  $p$  to  $\mu$  have been determined with considerable accuracy by Regnault. To determine  $J$  it is only required to measure the volume of saturated steam from a given weight of water; and the principal difficulty of the process lies in this determination, though the other quantities are also difficult of determination.

This volume can be calculated from the density of the vapor, but this is generally taken in the superheated state.

The experiments of Fairbairn and Tate\* are probably the best direct experiments on the density of saturated vapor, but even those do not pretend to a greater accuracy than about 1 in 100. With Regnault's values of the other quantities, they give about Joule's value for the equivalent, namely 425. Hirn, Herwig, and others have also made the determination, but the results do not agree very well. Herwig even used a Giessler standard thermometer, which I have shown to depart very much from the air thermometer.

Indeed, the experiments on this subject are so uncertain, that physicists have about concluded to use this method rather for the determination of the volume of saturated vapors than for the mechanical equivalent of heat.

*From the Steam-Engine and Expansion of Metals.*

The experiments of Hirn on the steam-engine and of Edlund on the expansion and contraction of metals, are very excellent as illustrat-

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\* Phil. Mag., ser. 4, xxi. 230.



ing the theory of the subject, but cannot have any weight as accurate determinations of the equivalent.

*From Friction Experiments.*

Experiments of this nature, that is, irreversible processes for converting mechanical energy into heat, give by far the best methods for the determination of the equivalent.

Rumford's experiment of 1798 is only valuable from an historical point of view. Joule's results since 1843 undoubtedly give the best data we yet have for the determination of the equivalent. The mean of all his friction experiments of 1847 and 1850 which are given in the table is 425.8, though he prefers the smallest number, 423.9, of 1850. This last number is at present accepted throughout the civilized world, though there is at present a tendency to consider the number too small. But this value and his recent result of 1878 have undoubtedly as much weight as all other results put together.

As sources of error in these determinations I would suggest, first, the use of the mercurial instead of the air thermometer. Joule compared his thermometers with one made by Fastré. In the *Appendix to Thermometry* I give the comparison of two thermometers made by Fastré in 1850, with the air thermometer, as well as of a large number of others. From this it seems that all thermometers as far as measured stand *above* the air thermometer between  $0^{\circ}$  and  $100^{\circ}$ , and that the average for the Fastré at  $40^{\circ}$  is about  $0^{\circ}.1$  C. Using the formula given in *Thermometry* this would produce an error of about 3 parts in 1,000 at  $15^{\circ}$  C., the temperature Joule used.

The specific heat of copper which Joule uses, namely, .09515, is undoubtedly too large. Using the value deduced from more recent experiments in calculating the capacity of my calorimeter, .0922, Joule's number would again be increased 13 parts in 10,000, so that we have, —

Joule's value . . . . .	423.9, water at $15^{\circ}.7$ C.
Reduction to air thermometer . .	+1.3
Correction for specific heat of copper	+ .5
“ to latitude of Baltimore	+ .5
	<u>426.2</u>

It does not seem improbable that this should be still further increased, seeing that the reduction to the air thermometer is the smallest admissible, as most other thermometers which I have measured give greater correction, and some even more than three times as great

as the one here used, and would thus bring the value even as high as 429.

One very serious defect in Joule's experiments is the small range of temperature used, this being only about half a degree Fahrenheit, or about six divisions on his thermometer. It would seem almost impossible to calibrate a thermometer so accurately that six divisions should be accurate to one per cent, and it would certainly need a very skilful observer to read to that degree of accuracy. Further, the same thermometer "A" was used throughout the whole experiment with water, and so the error of calibration was hardly eliminated, the temperature of the water being nearly the same. In the experiment on quicksilver another thermometer was used, and he then finds a higher result, 424.7, which, reduced as above, gives 427.0 at Baltimore.

The experiments on the friction of iron should be probably rejected on account of the large and uncertain correction for the energy given out in sound.

The recent experiments of 1878 give a value of 772.55, which reduced gives at Baltimore 426.2, the same as the other experiment.

The agreement of these reduced values with my value at the same temperature, namely 427.3, is certainly very remarkable, and shows what an accurate experimenter Joule must be to get with his simple apparatus results so near those from my elaborate apparatus, which almost grinds out accurate results without labor except in reduction. Indeed, the quantity is the same as I find at about 20° C.

The experiments of Hirn of 1860-61 seem to point to a value of the equivalent higher than that found by Joule, but the details of the experiment do not seem to have been published, and they certainly were not reduced to the air thermometer.

The method used by Violle in 1870 does not seem capable of accuracy, seeing that the heat lost by a disc in rapid rotation, and while carried to the calorimeter, must have been uncertain.

The experiments of Hirn are of much interest from the methods used, but can hardly have weight as accurate determinations. Some of the methods will be again referred to when I come to the description of apparatus.

#### *Method by Heat generated by Electric Current.*

The old experiments of Quintus Icilius or Lenz do not have any except historical value, seeing that Weber's measure of absolute resistance was certainly incorrect, and we now have no means of finding its error.

The theory of the process is as follows. The energy of electricity being the product of the potential by the quantity, the energy expended by forcing the quantity of electricity,  $Q$ , along a wire of resistance,  $R$ , in a second of time, must be  $Q^2 R$ , and as this must equal the mechanical equivalent of the heat generated, we must have  $JH = Q^2 R t$ , where  $H$  is the heat generated and  $t$  is the time the current  $Q$  flows.

The principal difficulty about the determination by this method seems to be that of finding  $R$  in absolute measure. A table of the values of the ohm as obtained by different observers, was published by me in my paper on the "Absolute Unit of Electrical Resistance," in the American Journal of Science, Vol. XV., and I here give it with some changes.

TABLE XXXI.

Date.	Observer.	Value of Ohm.	REMARKS.
1849	Kirchoff	.88 to .90	Approximately.
1851	Weber	.95 to .97	Approximately.
1862	Weber	$\left\{ \begin{array}{l} 1.088 \\ 1.075 \\ 1.0000 \end{array} \right.$	From Thomson's unit. From Weber's value of Siemens unit. Mean of all results.
1863-4	B. A. Committee	$\left\{ \begin{array}{l} 1.0000 \\ .993 \end{array} \right.$	Corrected by Rowland to zero velocity of coil.
1870	Kohlrausch	1.0198	
1873	Lorenz	.975	Approximately.
1876	Rowland	.9911*	From a preliminary comparison with the B. A. unit.
1878	H. F. Weber	1.0014	Using ratio of Siemens unit to ohm, .9536.

The ratio of the Siemens unit to the ohm is now generally taken at .9536, though previous to 1864 there seems to have been some doubt as to the value of the Siemens unit.

Since 1863-4, when units of resistance first began to be made with great accuracy, two determinations of the heat generated have been made. The first by Joule with the ohm, and the second by H. F. Weber, of Zurich, with the Siemens unit.

Each determination of resistance with each of these experiments gives one value of the mechanical equivalent. As Lorenz's result was only in illustration of a method, I have not included it among the exact determinations.

The result found by Joule was  $J = 25187$  in absolute measure

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\* Given .9912 by mistake in the other tables.

using feet and degrees F., which becomes 429.9 in degrees C. on a mercurial thermometer and in the latitude of Baltimore, compared with water at 18° C.

TABLE XXXII.—EXPERIMENTS OF JOULE.

Observer.	Value of B. A. Unit.	Mechanical Equivalent from Joule's Exp.	Mechanical Equivalent reduced to Air Thermometer and corrected for Sp. Ht. of Copper.
B. A. Committee .....	1.0000	429.9	431.4
Ditto corrected by Rowland	.993	426.9	428.4
Kohlrausch .....	1.0193	438.2	439.7
Rowland .....	.9911	426.1	427.6
H. F. Weber .....	1.0014	430.5	432.0

The experiments of H. F. Weber\* gave 428.15 in the latitude of Zurich and for 1° C. on the air thermometer and at a temperature of 18° C. This reduced to the latitude of Baltimore gives 428.45.

TABLE XXXIII.

EXPERIMENTS OF H. F. WEBER.			Mean of Joule and Weber, giving Joule twice the Weight of Weber.
Observer.	Value of B. A. Unit.	Mechanical Equivalent of Heat from Weber's Experiments.	Mean Equivalent re- duced to Air Thermom- eter in the Latitude of Baltimore.
B. A. Committee .....	1.000	427.9	430.2
Ditto corrected by Rowland	.993	424.9	427.2
Kohlrausch .....	1.0193	436.2	439.1
Rowland .....	.9911	424.1	426.4
H. F. Weber .....	1.0014	428.5	431.4

My own value at this temperature is 426.8, which agrees almost exactly with the fourth value from my own determination of the absolute unit.†

There can be no doubt that Joule's result is most exact, and hence I have given his results twice the weight of Weber's. Weber used a wire of about 14 ohms' resistance, and a small calorimeter holding only 250 grammes of water. This wire was apparently placed in the water without any insulating coating, and yet current enough was sent through

\* Phil. Mag., 1878, 5th ser., v. 135.

† The value of the ohm found by reversing the calculation would be .992, almost exactly my value.

it to heat the water  $15^{\circ}$  during the experiment. No precaution seems to have been taken as to the current passing into the water, which Joule accurately investigated. Again, the water does not seem to have been continuously stirred, which Joule found necessary. And further, Newton's law of cooling does not apply to so great a range as  $15^{\circ}$ , though the error from this source was probably small. Furthermore, I know of no platinum which has an increase of coefficient of .001054 for  $1^{\circ}$  C., but it is usually given at about .003.

There can be no doubt that experiments depending on the heating of a wire give too small a value of the equivalent, seeing that the temperature of the wire during the heating must always be higher than that of the water surrounding it, and hence more heat will be generated than there should be. Hence the numbers should be slightly *increased*. Joule used wire of platinum-silver alloy, and Weber platinum wire, which may account for Weber's finding a smaller value than Joule, and Weber's value would be more in error than Joule's. Undoubtedly this is a serious source of error, and I am about to repeat an experiment of this kind in which it is entirely avoided. Considering this source of error, these experiments confirm both my value of the ohm and of the mechanical equivalent, and unquestionably show a large error in Kohlrausch's absolute value of the Siemens unit or ohm.

The experiments of Joule and Favre, where the heat generated by a current, both when it does mechanical work and when it does not, are very interesting, but can hardly have any weight in an estimation of the true value of the equivalent.

The method of calculating the equivalent from the chemical action in a battery, or the electro-motive force required to decompose any substance, such as water, is as follows.

Let  $E$  be such electro-motive force and  $c$  be the quantity of chemical substance formed in battery or decomposed in voltameter per second. Then total energy of current of energy per second is  $E Q$ , where  $Q$  is the current, or  $c Q H J$ , where  $H$  is the heat generated by unit of  $c$ , or required to decompose unit of  $c$ . Hence, if the process is entirely reversible, we must have in either case

$$C H J = E.$$

But the process is not always reversible, seeing that it requires more electro-motive force to decompose water than is given by a gas battery. This is probably due to the formation at first of some unstable compound like ozone. The process with a battery seems to be

best, and we can thus apply it to the Daniell cell. The following quantities are mostly taken from Kohlrausch.

The quantity  $c$  has been found by various observers, and Kohlrausch\* gives the mean value as .009421 for water according to his units (mg., mm., second system). Therefore for hydrogen it is .001047.

The quantity  $H$  can be observed directly by short-circuiting the battery, or can be found from experiments like those of Favre and Silbermann.

The electro-motive force  $E$  can be made to depend either upon the absolute measure of resistance, or can be determined, as Thomson has done, in electro-static units. In electro-magnetic units it is

	Siemens.	Ohms.	Absolute Measure according to my Determination.
After Waltenhofen	11.43	10.90	$10.80 \times 10^{10}$
" Kohlrausch †	11.71	11.17	$11.07 \times 10^{10}$

After Favre, 1 equivalent of zinc develops in the Daniell cell 23993 heat units;

$$\therefore \frac{J}{g} = \frac{E}{cHg}.$$

On the mg., mm., second system, we have  $E = 10.935 \times 10^{10}$ ,  $c = .001047$ ,  $H = 23993$ ,  $g = 9800.5$  at Baltimore.

$$\therefore \frac{J}{g} = 444160^{\text{mm.}} = 444.2 \text{ meters.}$$

Using Kohlrausch's value for absolute resistance, he finds 456.5, which is much more in error than that from my determination. I do not give the calculation from the Grove battery, because the Grove battery is not reversible, and action takes place in it even when no current flows.

Thomson finds the difference of potential between the poles of a Daniell cell in electro-static measure to be .00374 on the cm., gram., second system. ‡ Using the ratio 29,900 000 000<sup>cm.</sup> per second, as I have recently found, but not yet published, we have 111 800 000 on the electro-magnetic system or  $11.18 \times 10^{10}$  on the mm., mg., second system. This gives

$$\frac{J}{g} = 474.3 \text{ meters.}$$

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\* Pogg. Ann., cxlix. 179.

† Given by Kohlrausch, Pogg. Ann., cxlix. 182.

‡ Thomson, Papers on Electrostatics and Magnetism, p. 246.

*General Criticism.*

All the results so far obtained, except those of Joule, seem to be of the crudest description; and even when care was apparently taken in the experiment, the method seems to be defective, or the determination is made to rest upon the determination of some other constant whose value is not accurately known. Again, only one or two observers have compared their thermometers with the air thermometer, although I have shown in "Thermometry" that an error of more than one per cent may be made by this method. The range of temperatures is also small as a general rule and the specific heat of water is assumed constant.

Hence a new determination, avoiding these sources of error, seems to be imperatively demanded.

*(b.) Description of Apparatus.*

## 1. PRELIMINARY REMARKS.

As we have seen in the historical portion, the only experiments of a high degree of accuracy to the present time are those of Joule. Looked at from a general point of view, the principal defects of his method were the use of the mercurial instead of the air thermometer, and the small rate at which the temperature of his calorimeter rose.

In devising a new method a great rise of temperature in a short time was considered to be the great point, combined, of course, with an accurate measurement of the work done. For a great rise of temperature great work must be done, which necessitates the use of a steam-engine or other motive power. For the measurement of the work done, there is only one principle in use at present, which is, that the work transmitted by any shaft in a given time is equal to  $2\pi$  times the product of the moment of the force by the number of revolutions of the shaft in that time.

In mechanics it is common to measure the amount of the force twisting the shaft by breaking it at the given point, and attaching the two ends together by some arrangement of springs whose stretching gives the moment. Morin's dynamometer is an example. Hirn\* gives a method which he seems to consider new, but which is immediately recognized as Huyghens's arrangement for winding clocks with-

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\* Exposition de la Théorie Mécanique de la Chaleur, 8<sup>me</sup> éd., p. 18.

out stopping them. As cords and pulleys are used which may slip on each other, it cannot possess much accuracy. I have devised a method by cog-wheels which is more accurate, but which is better adapted for use in the machine-shop than for scientific experimentation.

But the most accurate method known to engineers for measuring the work of an engine is that of White's friction brake, and on this I have based my apparatus. Hirn was the first to use this principle in determining the mechanical equivalent of heat. In his experiment a horizontal axis was turned by a steam-engine. On the axis was a pulley with a flat surface, on which rested a piece of bronze which was to be heated by the friction. The moment of the force with which the friction tended to turn the piece of bronze was measured, together with the velocity of revolution. This experiment, which Hirn calls a *balance de frottement*, was first constructed by him to test the quality of oils used in the industrial arts. He experimented by passing a current of water through the apparatus and observing the temperature of the water before and after passing through. He thus obtained a rough approximation to Joule's equivalent.

He afterwards constructed an apparatus consisting of two cylinders about 30<sup>cm.</sup> in diameter and 100<sup>cm.</sup> long, turning one within the other, the annular space between which could be filled with water, or through which a stream of water could be made to flow whose temperature could be measured before and after. The work was measured by the same method as before.

But in neither of these methods does Hirn seem to have recognized the principle of the work transmitted by a shaft being equal to the moment of the force multiplied by the angle of rotation of the shaft. In designing his apparatus, he evidently had in view the reproduction in circular motion of the case of friction between two planes in linear motion.

Since I designed my apparatus, Puluj\* has designed an instrument to be worked by hand, and based on the principle used by Hirn. He places the revolving axis vertical, and the friction part consists of two cones rubbing together. But no new principle is involved in his apparatus further than in that used by Hirn.†

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\* Pogg. Ann., clvii. 487.

† Joule's latest results were published after this was written, and I was not aware that he had made this improvement until lately. The result of his experiment, however, reached me soon after, and I have referred to it in the paper, but I did not see the complete paper until much later.



In my apparatus one of the new features has been the introduction of the Joule calorimeter in the place of the friction cylinders of Hirn or the cones of Puluij. At first sight the currents and whirlpools in such a calorimeter might be supposed to have some effect; but when the motion is steady, it is readily seen that the torsion of the calorimeter is equal to that of the shaft, and hence the principle must apply.

This change, together with the other new features in the experiments and apparatus, has at once made the method one of extreme accuracy, surpassing all others very many fold.

## 2. GENERAL DESCRIPTION.

The apparatus was situated in a small building, entirely separate from the other University buildings, and where it was free from disturbances.

Fig. 6 gives a general view of the apparatus. To a movable axis,  $a b$ , a calorimeter similar to Joule's is attached, and the whole is suspended by a torsion wire,  $c$ . The shaft of the calorimeter comes out from the bottom, and is attached to a shaft,  $e f$ , which receives a uniform motion from the engine by means of the bevel wheels  $g$  and  $h$ . To the axis,  $a b$ , an accurately turned wheel,  $k l$ , was attached, and the moment of the force tending to turn the calorimeter was measured by the weights  $o$  and  $p$ , attached to silk tapes passing around the circumference of this wheel in combination with the torsion of the suspending wire. To this axis was also attached a long arm, having two sliding weights,  $q$  and  $r$ , by which the moment of inertia could be varied or determined.

The number of revolutions was determined by a chronograph, which received motion by a screw on the shaft  $e f$ , and which made one revolution for 102 of the shaft. On this chronograph was recorded the transit of the mercury over the divisions of the thermometer.

Around the calorimeter a water jacket,  $t u$ , made in halves, was placed, so that the radiation could be estimated. A wooden box surrounded the whole, to shield the observer from the calorimeter.

The action of the apparatus is in general as follows. As the inner paddles revolve, the water strikes against the outer paddles, and so tends to turn the calorimeter. When this force is balanced by the weights  $o p$ , the whole will be in equilibrium, which is rendered stable by the torsion of the wire  $c d$ . Should any slight change take place in the velocity, the calorimeter will revolve in one direction or the other until the torsion brings it into equilibrium again. The amount

of torsion read off on a scale on the edge of  $kl$  gives the correction to be added to or subtracted from the weights  $op$ .

One observer constantly reads the circle  $k l$ , and the other constantly records the transits of the mercury over the divisions of the thermometer.

A series extending over from one half to a whole hour, and recording a rise of  $15^{\circ}$  C. to perhaps  $25^{\circ}$  C., and in which a record was made for perhaps each tenth of a degree, would thus contain several hundred observations, from any two of which the equivalent of heat could be determined, though they would not all be independent. Such a series would evidently have immense weight; and, in fact, I estimate that, neglecting constant errors, a single series has more weight than all of Joule's experiments of 1849, on water, put together.\*

The correction for radiation is inversely proportional to the ratio of the rate of work generated to the rate at which the heat is lost; and this for equal ranges of temperature is only  $\frac{1}{20}$  as great in my measures as in Joule's; for Joule's rate of increase was about  $0^{\circ}.62$  C. per hour, while mine is about  $35^{\circ}$  C. in the same time, and can be increased to over  $45^{\circ}$  C. per hour.

### 3. DETAILS.

#### *The Calorimeter.*

Joule's calorimeter was made in a very simple manner, with few paddles, and without reference to the production of currents to mix up the water. Hence the paddles were made without solder, and were screwed together. Indeed, there was no solder about the apparatus.

But, for my purpose, the number of paddles must be multiplied, so that there shall be no jerk in the motion, and that the resistance may be great: they must be stronger, to resist the force from the engine, and they must be light, so as not to add an uncertain quantity to the calorific capacity. Besides this, the shape must be such as to cause the whole of the water to run in a constant stream past the thermometer, and to cause constant exchange between the water at the top and at the bottom.

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\* Forty experiments, with an average rise of temperature of  $0^{\circ}.56$  F., equal to  $0^{\circ}.31$  C., gives a total rise of  $12^{\circ}.4$  C., which is only about two thirds the average of one of my experiments. As my work is measured with equal accuracy, and my radiation with greater, the statement seems to be correct.

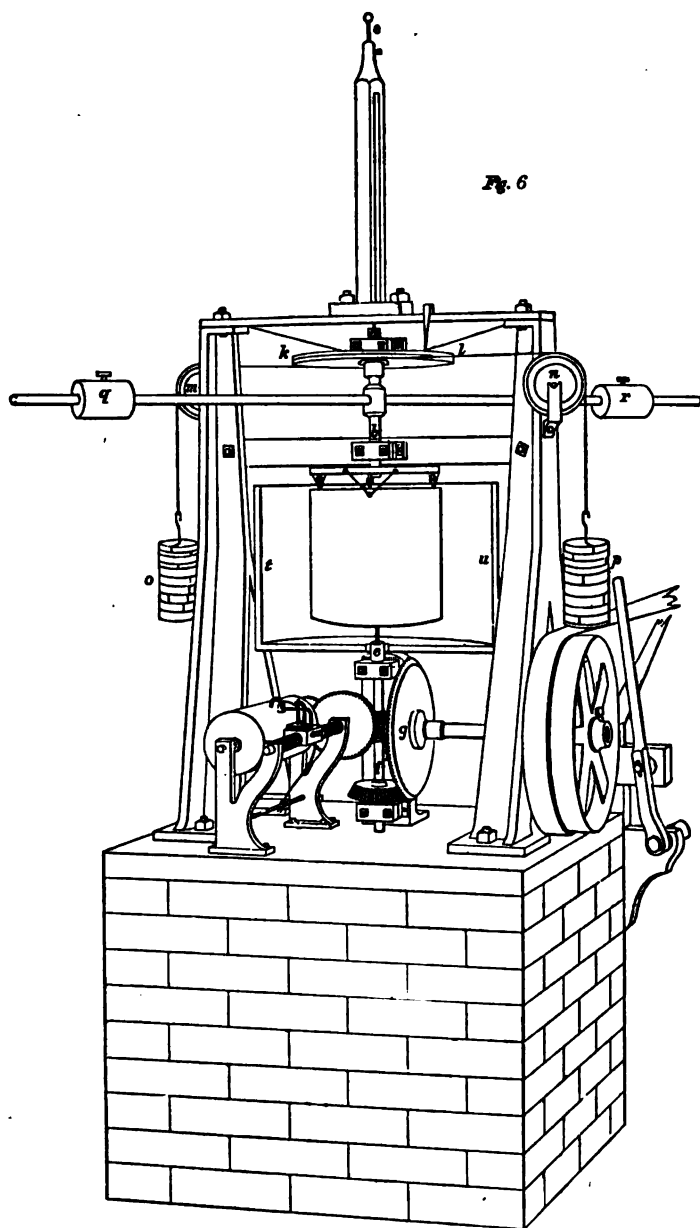


Fig. 7 shows a section of the calorimeter, and Fig. 8 a perspective view of the revolving paddles removed from the apparatus, and with the exterior paddles removed from around it; which could not, however, be accomplished physically without destroying them.

To the axis *c b*, Fig. 7, which was of steel, and 6<sup>mm</sup>. in diameter, a copper cylinder, *a d*, was attached, by means of four stout wires at *e*, and four more at *f*. To this cylinder four rings, *g, h, i, j*, were attached, which supported the paddles. Each one had eight paddles, but each ring was displaced through a small angle with reference to

Fig. 7.

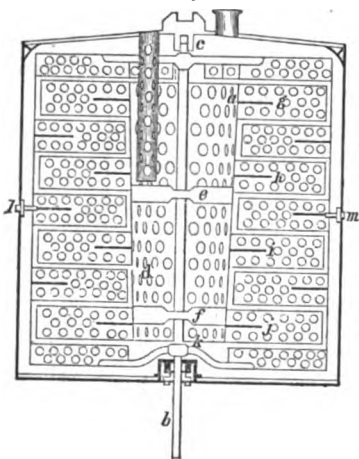
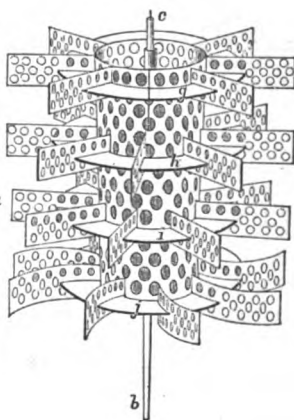


Fig. 8.



the one below it, so that no one paddle came over another. This was to make the resistance continuous, and not periodical. The lower row of paddles were turned backwards, so that they had a tendency to throw the water outwards and make the circulation, as I shall show afterwards.

Around these movable paddles were the stationary paddles, consisting of five rows of ten each. These were attached to the movable paddles by bearings, at the points *c* and *k*, of the shaft, and were removed with the latter when this was taken from the calorimeter. When the whole was placed in the calorimeter, these outer paddles were attached to it by means of four screws, *l* and *m*, so as to be immovable.

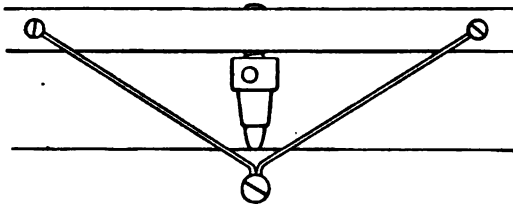
The cover of the calorimeter was attached to a brass ring, which was nicely ground to another brass ring on the calorimeter, and which

could be made perfectly tight by means of a little white-lead paint. The shaft passed through a stuffing-box at the bottom, which was entirely within the outer surface of the calorimeter, so that the heat generated should all go to the water. The upper end of the shaft rested in a bearing in a piece of brass attached to the cover. In the cover there were two openings,—one for the thermometer, and the other for filling the calorimeter with water.

From the opening for the thermometer, a tube of copper, perforated with large holes, descended nearly to the centre of the calorimeter. The thermometer was in this sieve-like tube at only a short distance from the centre of the calorimeter, with the revolving paddles outside of it, and in the stream of water, which circulated as shown by the arrows.

This circulation of water took place as follows. The lower paddles threw the water violently outwards, while the upper paddles were

*Fig. 9.*



prevented from doing so by a cylinder surrounding the fixed paddles. The consequence was, that the water flowed up in the space between the outer shell and the fixed paddles, and down through the central tube of the revolving paddles. As there was always a little air at the top to allow for expansion, it would also aid in the same direction. These currents, which were very violent, could be observed through the openings.

The calorimeter was attached to a wheel, fixed to the shaft *a b*, by the method shown in Fig. 9. At the edge of the wheel, which was of the exact diameter of the calorimeter, two screws were attached, from which wires descended to a single screw in the edge of the calorimeter. Through the wheel, a screw armed with a vulcanite point pressed upon the calorimeter, and held it firmly. Three of these arrangements, at distances of  $120^\circ$ , were used. To centre the calorimeter, a piece of vulcanite at the centre was used. By this method of suspension very little heat could escape, and the amount could be allowed for by the radiation experiments.

*The Torsion System.*

The torsion wire was of such strength that one millimeter on the scale at the edge of the wheel signified 11.8 grammes, or about  $\frac{1}{80}$  of the weights *o p* generally used. There were stops on the wheel, so that it could not move through more than a small angle. The weights were suspended by very flexible silk tapes, 6<sup>mm</sup>. or 8<sup>mm</sup>. broad and 0.3<sup>mm</sup>. thick. They varied from 4.5<sup>k</sup> to 8.5<sup>k</sup> taken together. The shaft, *a b*, was of uniform size throughout, so that the wire *c* suspended the whole system, and no weight rested on the bearings.

The pulleys, *m, n*, Fig. 6, were very exactly turned and balanced, and the whole suspended system was so free as to vibrate for a considerable time. However, as will be shown hereafter, its freedom is of little consequence.

*The Water Jacket.*

Around the calorimeter, a water jacket, *t u*, was placed, so that the radiation should be perfectly definite. During the preliminary experiments a simple tin jacket was used, whose temperature was determined by two thermometers, one above and the other below, inserted in tubes attached to the jacket.

*The Driving Gear.*

The cog-wheels, *g, h*, were made by Messrs. Brown and Sharpe, of Providence, and were so well cut that the motion transmitted to the calorimeter must have been very uniform.

*The Chronograph.*

The cylinder of the chronograph was turned by a screw on the shaft *e f*, and received one revolution for 102 of the paddles; 155 revolutions of the cylinder, or 15,810 of the paddles, could be recorded, though, when necessary, the paper could be changed without stopping, and the experiment thus continued without interruption.

*The Frame and Foundation.*

The frame was very massive and strong, so as to prevent oscillation; and the whole instrument weighed about 500 pounds as nearly as could be estimated. It was placed on a solid brick pier, with a firm foundation in the ground. The trembling was barely perceptible to the hand when running the fastest.

*The Engine.*

The driving power was a petroleum engine, which was very efficient in driving the apparatus with uniformity.

*The Balance.*

For weighing the calorimeter, a balance capable of showing the presence of less than  $\frac{1}{10}$  gramme with 15,000 grammes was used. The weights, however, by Schickert, of Dresden, were accurate among themselves to at least  $5^{th}$  for the larger weights, and in proportion for the smaller. A more accurate balance would have been useless, as will be seen further on.

*Adjustments.*

There are few adjustments, and they were principally made in the construction.

In the first place, the shafts  $ab$  and  $ef$  must be on line. Secondly, the wheels  $m$   $n$  must be so adjusted that their planes are vertical, and that the tapes shall pass over them symmetrically, and that their edges shall be in the plane of the wheel  $kl$ .

Deviation from these adjustments only produced small error.

*(c.) Theory of the Experiment.*

## 1. ESTIMATION OF WORK DONE.

The calorimeter is constantly receiving heat from the friction, and is giving out heat by radiation and conduction. Now, at any given instant of time, the temperature of the whole of the calorimeter is not the same. Owing to the violent stirring, the water is undoubtedly at a very uniform temperature throughout. But the solid parts of the calorimeter cannot be so. The greatest difference of temperature is evidently soon after the commencement of the operation. But after some time the apparatus reaches a stationary state, in which, but for the radiation, the rise of temperature at all points would be the same. This steady state will be theoretically reached only after an infinite time; but as most of the metal is copper, and quite thin, and as the whole capacity of the metal work is only about four per cent of the total capacity, I have thought that one or two minutes was enough to allow, though, if others do not think this time sufficient, they can readily reject the first few observations of each series. When there is radiation, the stationary state will never be reached theoretically,

though practically there is little difference from the case where there is no radiation.

The measurement of the work done can be computed as follows. Let  $M$  be the moment of the force tending to turn the calorimeter, and  $d\theta$  the angle moved by the shaft. The work done in the time  $t$  will be  $\int M d\theta$ . If the moment of the force is constant, the integral is simply  $M\theta$ ; but it is impossible to obtain an engine which runs with perfect steadiness, and although we may be able to calculate the integral, as far as long periods are concerned, by observation of the torsion circle, yet we are not thus able to allow for the irregularity during one revolution of the engine. Hence I have devised the following theory. I have found, by experiments with the instrument, that the moment of the force is very nearly, for high velocities at least, proportional to the square of the velocity. For rapid changes of the velocity, this is not exactly true, but as the paddles are very numerous in the calorimeter, it is probably very nearly true. We have then

$$M = C \left( \frac{d\theta}{dt} \right)^2,$$

where  $C$  is a constant. Hence the work done becomes

$$w = C \int \left( \frac{d\theta}{dt} \right)^2 d\theta = C \int \left( \frac{d\theta}{dt} \right)^3 dt.$$

As we allow for irregularities of long period by readings of the torsion circle, we can assume in this investigation that the mean velocity is constant, and equal to  $v_0$ . The form of the variation of the velocity must be assumed, and I shall put, without further discussion,

$$\frac{d\theta}{dt} = v_0 \left( 1 + c \cos \frac{2\pi t}{a} \right).$$

We then find, on integrating from  $a$  to 0,

$$w = C v_0^3 a \left( 1 + \frac{3}{2} c^2 \right),$$

which is the work on the calorimeter during one revolution of the engine.

The equation of the motion of the calorimeter, supposing it to be nearly stationary, and neglecting the change of torsion of the suspending wire, is

$$\frac{m}{g} \frac{d^2 \psi}{dt^2} - \frac{W D}{2} + C v_0^2 \left( 1 + c \cos \frac{2\pi t}{a} \right)^2 = 0,$$

where  $m$  is the moment of inertia of the calorimeter and its attachments,  $\psi$  is the angular position of the calorimeter,  $W$  is the sum of



the torsion weights, and  $D$  is the diameter of the torsion wheel. Hence,

$$\psi - \psi_0 = \frac{2}{\pi} \left\{ \frac{1}{2} t [C v_0^2 (1 + \frac{1}{2} c^2) - W D] + C v_0^2 \left[ \frac{a^2 c^2}{16 \pi^2} \sin^2 \frac{2 \pi t}{a} - \frac{a^2 c}{2 \pi^2} \left( \cos \frac{2 \pi t}{a} \right) \right] \right\}.$$

When  $W D = 2 C v_0^2 (1 + \frac{1}{2} c^2)$ , the calorimeter will merely oscillate around a given position, and will reach its maximum at the times  $t = 0, \frac{1}{2} a, a, \&c.$

The total amplitude of each oscillation will be very nearly

$$\psi - \psi' = \frac{C v_0^2 g a^2 c}{\pi^2 m} = \frac{W D g a^2 c}{2 \pi^2 m}.$$

If  $x$  is the amplitude of each oscillation, as measured in millimeters, on the edge of the wheel of diameter  $D$ , we have  $\psi - \psi' = \frac{2 x}{D}$ .

Hence,

$$c = \frac{1}{2} \frac{\pi x n^2}{C D g},$$

where  $n$  is the number of revolutions of the engine per second.

Having found  $c$  in this way, the work will be, during any time,

$$w = \pi W D N (1 + c^2),$$

where  $N$  is the total number of revolutions of the *paddles*.

A variation of the velocity of ten per cent from the mean, or twenty per cent total, would thus only cause an error of one per cent in the equivalent.

Hence, although the engine was only single acting, yet it ran easily, had great excess of power, and was very constant as far as long periods were concerned. The engine ran very fast, making from 200 to 250 revolutions per minute. The fly-wheel weighed about 220 pounds, and had a radius of  $1\frac{1}{4}$  feet. At four turns per second, this gives an energy of about 8400 foot pounds stored in the wheel. The calorimeter required about one-half horse-power to drive it; and, assuming the same for the engine friction, we have about 140 foot pounds of work required per revolution. Taking the most unfavorable case, where all the power is given to the engine at one point, the velocity changes during the revolution about four per cent, or  $c$  would nearly equal .02, causing an error of 1 part in 2500 nearly. By means of the shaking of the calorimeter, I have estimated  $c$  as follows, the value of  $m$  being changed by changing the weight on the inertia bar, or taking it off altogether. The estimate of the shaking was made by two persons independently.

m.	$x$ observed.	$c$ calculated.
2,200,000 grms. cm. <sup>2</sup>	.6 mm.	.016
3,100,000 "	.36 "	.013
11,800,000 "	.13 "	.017
Mean,		$c = .015$

causing a correction of 1 part in 5000.

Another method of estimating the irregularity of running is to put on or take off weights until the calorimeter rests so firmly against the stops that the vibration ceases. Estimated in this way, I have found a little larger value of  $c$ , namely, about .017.

But as one cannot be too careful about such sources of error, I have experimented on the equivalent with different velocities and with very different ways of running the engine, by which  $c$  was greatly changed, and so have satisfied myself that the correction from this source is inappreciable in the present state of the science of heat.

Hence I shall simply put for the work

$$w = \pi N W D,$$

in gravitation measure at Baltimore. To reduce to absolute measure, we must multiply by the force of gravity given by the formula

$$g = 9.78009 + .0506 \sin^2 \phi,$$

which gives 9.8005 meters per second at Baltimore. If the calorimeter moved without friction, no work would be required to cause it to vibrate back and forth, as I have described; but when it moves *with* friction, some work is required. When I designed the apparatus, I thus had an idea that it would be best to make it as immovable as possible by adding to its moment of inertia by means of the inertia bar and weights. But on considering the subject further, I see that only the excess of energy represented by  $c^2 \pi N W D$  can be used in this way. For, when the calorimeter is rendered nearly immovable by its great moment of inertia, the work done on it is, as we have seen,  $\pi N W D (1 + c^2)$ ; but if it had no inertia, it is evident that the work would be only  $\pi N W D$ . If, therefore, the calorimeter is made partially stationary, either by its moment of inertia or by friction, the work will be somewhere between these two, and the work spent in friction will be only so much taken from the error. Hence in the latter experiments the inertia bar was taken off, and then the calorimeter constantly vibrated through about half a millimeter on the torsion scale.

Besides this quick vibration, the calorimeter is constantly moving to

the extent of a few millimeters back and forth, according to the varying velocity of the engine. As frequent readings were taken, these changes were eliminated. In very rare cases the weights had to be changed during the experiment; but this was very seldom.

The vibration and irregular motion of the calorimeter back and forth served a very useful purpose, inasmuch as it caused the friction of the torsion apparatus to act first in one direction and then in the other, so that it was finally eliminated. The torsion apparatus moved very freely when the calorimeter was not in position, and would keep vibrating for some minutes by itself, but with the calorimeter there was necessarily some binding. But the vibration made it so free that it would return quickly to its exact position of equilibrium when drawn aside, and would also quickly show any small addition to the weights. This was tried in each experiment.

To measure the heat generated, we require to know the calorific capacity of the whole calorimeter, and the rise of temperature which would have taken place provided no heat had been lost by radiation. The capacity of the calorimeter alone I have discussed elsewhere, finding the total amount equal to  $.347^k$  of water at ordinary temperatures. The total capacity of the calorimeter is then  $A + .347$ , where  $A$  is the weight of water. Hence Joule's equivalent in absolute measure is

$$J = \frac{102 \pi n W D}{(A + .347) (t - t')} g,$$

where  $n$  is the number of revolutions of the chronograph, it making one revolution to 102 of the paddles.

The corrections needed are as follows:—

1st. Correction for weighing in air. This must be made to  $W$ , the cast-iron weights, and to  $A + .347$ , the water and copper of the calorimeter. If  $\lambda$  is the density of the air under the given conditions, the correction is  $-.835 \lambda$ .

2d. For the weight of the tape by which the weights are hung. This is  $\frac{.0006}{W}$ .

3d. For the expansion of torsion wheel,  $D'$  being the diameter at  $20^\circ$  C. This is  $.000018 (t'' - 20)$ . Hence,

$$J = 102 \pi g \frac{n W D'}{(A + .347) (t - t')} \left( 1 + .000018 (t'' - 20) + \frac{.0006}{W} - .835 \lambda \right),$$

where  $t - t'$  is the rise of the temperature corrected for radiation.

## 2. RADIATION.

The correction for radiation varies, of course, with the difference of temperature between the calorimeter and jacket; but, owing to the rapid generation of heat, the correction is generally small in proportion. The temperature generated was generally about  $0^{\circ}.6$  per minute. The loss of temperature per minute by radiation was approximately  $.0014 \theta^{\circ}$  per minute, where  $\theta$  is the difference of the temperature. This is one per cent for  $10^{\circ}.7$ , and four per cent for  $14^{\circ}.2$ . Generally, the calorimeter was cooler than the jacket to start with, and so a rise of about  $20^{\circ}$  could be accomplished without a rate of correction at any point of more than four per cent, and an average correction of less than two per cent. An error of ten per cent is thus required in the estimation of the radiation to produce an average error of 1 in 500, or 1 in 250 at a single point. The coefficients never differ from the mean more than about two per cent. The observations on the equivalent, being at a great variety of temperatures, check each other as to any error in the radiation.

The losses of heat which I place under the head of radiation include conduction and convection as well. I divide the losses of heat into the following parts: 1st. Conduction down the shaft; 2d. Conduction by means of the suspending wires or vulcanite points to the wheel above; 3d. True radiation; 4th. Convection by the air. To get some idea of the relative amounts lost in this way, we can calculate the loss by conduction from the known coefficients of conduction, and we can get some idea of the relative loss from a polished surface from the experiments of Mr. Nichol. In this way I suppose the total coefficient of radiation to be made up approximately as follows:—

Conduction along shaft	. . . . .	.00011
“ “ suspending wires	. . . . .	.00006
True radiation	. . . . .	.00017
Convection	. . . . .	.00106
Total	. . . . .	<u>.00140</u>

The conduction through the vulcanite only amounts to .0000002.

From this it would seem that three fourths of the loss is due to radiation and convection combined.

The last two losses depend upon the difference of temperature between the calorimeter and the jacket, but the first two upon the difference between the calorimeter and frame of the machine and the wheel respectively. The frame was *always* of very nearly the same

temperature as the water jacket, but the wheel was usually slightly above it. At first its temperature was noted by a thermometer, and the loss to it computed separately; but it was found to be unnecessary, and finally the whole was assumed to be a function of the temperature of the calorimeter and of the jacket only.

At first sight it might seem that there was a source of error in having a journal so near the bottom of the calorimeter, and joined to it by a shaft. But if we consider it a moment, we shall see that the error is inappreciable; for even if there was friction enough in the journal to heat it as fast as the calorimeter, it would decrease the radiation only seven per cent, or make an average error in the experiment of only 1 in 700. But, in fact, the journal was very perfectly made, and there was no strain on it to produce friction; besides which, it was connected to a large mass of cast-iron which was attached to the base. Hence, as a matter of fact, the journal was not appreciably warmer after running than before, although tested by a thermometer. The difference could not have been more than a degree or so at most.

The warming of the wheel by conduction and of the journal by friction would tend to neutralize each other, as the wheel would be warmer and the journal cooler during the radiation experiment than the friction experiment.

The usual method of obtaining the coefficient of radiation would be to stop the engine while the calorimeter was hot, and observe the cooling, stirring the water occasionally when the temperature was read. This method I used at first, reading the temperature at intervals of about a half to a whole hour. But on thinking the matter over, it became apparent that the coefficient found in this way would be too small, especially at small differences of temperature; for the layer next to the outside would be cooled lower than the mean temperature, and the heat could only get to the outside by conduction through the water or by convection currents.

Hence I arranged the engine so as to run the paddles very slowly, so as to stir the water constantly, taking account of the number of the revolutions and the torsion, so as to compute the work. As I had foreseen, the results in this case were higher than by the other method. At low temperatures the error of the first method was fifteen per cent; but at high, it did not amount to more than about three to five per cent, and probably at *very* high temperatures it would almost vanish.

I do not consider it necessary to give all the details of the radiation experiments, but will merely remark that, as the calorimeter was

nickel-plated, and as seventy-five per cent of the so-called radiation is due to convection by the air, the coefficients of radiation were found to be very constant under similar conditions, even after long intervals of time.

The experiments were divided into two groups; one when the temperature of the jacket was about 5° C., and the other when it averaged about 20° C.

The results were then plotted, and the mean curve drawn through them, from which the following coefficients were obtained. These coefficients are the loss of temperature per minute, and per degree difference of temperature.

TABLE XXXV.—COEFFICIENTS OF RADIATION.

Difference between Jacket and Calorimeter.	Jacket 5°.	Jacket 20°.
—5	.00188	.00184
0	.00185	.00180
+5	.00187	.00182
10	.00142	.00188
15	.00148	.00144
20	.00154	.00150
25	.00158	.00154

As the quantity of water in the calorimeter sometimes varied slightly, the numbers should be modified to suit, they being true when the total capacity of the calorimeter was 8.75 kil. The total surface of the calorimeter was about 2350 sq. cm., and the unit of time *one minute*. To compare my results with those of McFarlane and of Nichol given in the Proc. R. S. and Proc. R. S. E., I will reduce my results so that they can be compared with the tables given by Professor Everett in his "Illustrations of the Centimeter-Gramme-Second System of Units," pp. 50, 51.

The reducing factor is .0621, and hence the last results for the jacket at 20° C. become:—

TABLE XXXVI.

Difference of Temperature.	Coefficient of Radiation on the C. G. S. System.	McFarlane's Value.	Ratio.
0	.000081	.000168	2.07
5	.000082	.000178	2.17
10	.000086	.000186	2.16
15	.000089	.000193	2.17
20	.000098	.000201	2.16
25	.000096	.000207	2.15

The variation which I find is almost exactly that given by McFarlane, as is shown by the constancy of the column of ratios. But my coefficients are less than half those of McFarlane. This may possibly be due to the fact that the walls of McFarlane's enclosure were blackened, and to his surface being of polished copper and mine of polished nickel: his surface may also have been better adapted by its form to the loss of heat by convection. The results of Nichol are also much lower than those of McFarlane.

The fact that the coefficients of radiation are less with increased temperature of jacket is just contrary to what Dulong and Petit found for radiation. But as I have shown that convection is the principal factor, I am at a loss to check my result with any other observer. Dulong and Petit make the loss from convection dependent only upon the difference of temperature, and approximately upon the square root of the pressure of the gas. Theoretically it would seem that the loss should be less as the mean temperature rises, seeing that the air becomes less dense and its viscosity increases. Should we substitute density for pressure in Dulong's law, we should have the loss by convection inversely as the square root of the mean absolute temperature, or approximately the absolute temperature of the jacket. This would give a decrease of one per cent in the radiation for about  $6^{\circ}$ , which is not far from what I have found.

To estimate the accuracy with which the radiation has been obtained is a very difficult matter, for the circumstances in the experiment are not the same as when the radiation was obtained. In the first place, although the water is stirred during the radiation, yet it is not stirred so violently as during the experiment. Further, the wheel above the calorimeter is warmer during radiation than during the experiment. Both these sources of error tend to give *too small* coefficients of radiation, and this is confirmed by looking over the final tables. But I have not felt at liberty to make any corrections based on the final results, as that would destroy the independence of the observations. But we are able thus to get the limits of the error produced.

During the preliminary experiments a water jacket was not used, but only a tin case, whose temperature was noted by a thermometer above and below. The radiation under these circumstances was larger, as the case was not entirely closed at the bottom, and so permitted more circulation of air.

### 3. CORRECTIONS TO THERMOMETERS, ETC.

Among the other corrections to the temperature as read off from the thermometers, the correction for the stem at the temperature of

the air is the greatest. The ordinary formula for the correction is  $.000156 n (t - t'')$ . But, in applying this correction, it is difficult to estimate  $n$ , the number of degrees of thermometer outside the calorimeter and at the temperature of the air, seeing that part of the stem is heated by conduction. The uncertainty vanishes as the thermometer becomes longer and longer, or rather as it is more and more sensitive. But even then some of the uncertainty remains. I have sought to avoid this uncertainty by placing a short tube filled with water about the lower part of the thermometer as it comes out of the calorimeter. The temperature of this was indicated by a thermometer, by aid of which also the heat lost to the water by conduction through the thermometer stem could be computed; this, however, was very minute compared with the whole heat generated, say 1 in 10,000.

The water being very nearly at the temperature of the air, the stem above it could be assumed to be at the temperature of the air indicated by a thermometer hung within an inch or two of it. The correction for stem would thus have to be divided into two parts, and calculated separately. Calculated in this way, I suppose the correction is perfectly certain to much less than one hundredth of a degree: the total amount was seldom over one tenth of a degree.

Among the uncertain errors to which the measurement of temperature is subjected, I may mention the following:—

1. Pressure on bulb. A pressure of 60<sup>cm.</sup> of water produced a change of about 0°.01 in the thermometers. When the calorimeter was entirely closed there was soon some pressure generated. Hence the introduction of the safety-tube,—a tube of thin glass about 10<sup>cm.</sup> long, extending through a cork in the top of the calorimeter. The top of the safety-tube was nearly closed by a cork to prevent evaporation. Had the tube been shorter, water would have been forced out, as well as air.

2. Conduction along stem from outside to thermometer bulb. To avoid this, not only was the bulb immersed, but also quite a length of stem. As this portion of the stem, as also the bulb, was surrounded by water in violent motion, there could have been no large error from this source. The immersed stem to the top of the bulb was generally about 5<sup>cm.</sup> or more, and the stem only about .8<sup>cm.</sup> in diameter.

3. The thermometer is never at the temperature of the water, because the latter is constantly rising; but we do not assume that it is so in the experiment. We only assume that it lags behind the water to the same amount at all parts of the experiment, and this is doubtless true.



To see if the amount was appreciable, I suddenly threw the apparatus out of gear, thus stopping it. The temperature was observed to continue rising about  $0^{\circ}.02$  C. Allowing  $0^{\circ}.01$  for the rise due to motion after the word "Stop" was given, we have about  $0^{\circ}.01$  C. as the amount the thermometer lagged behind the water.

4. Evaporation. A possible source of error exists in the cooling of the calorimeter by evaporation of water leaking out from it.

The water was always weighed before and after the experiment in a balance giving  $\frac{1}{10}$  gramme with accuracy. The normal amount of loss from removal of thermometer, wet corks, &c. was about 1 gramme. The calorimeter was perfectly tight, and had no leakage at any point in its normal state. Once or twice the screws of the stuffing-box worked loose, but these experiments were rejected.

The evaporation of 1 gramme of water requires about 600 heat units, which is sufficient to depress the temperature of the calorimeter about  $0^{\circ}.07$  C. As the only point at which evaporation could take place was through a hole less than  $1^{\text{mm}}$  diameter in the safety-tube, I think it is reasonable to assume that the error from this source is inappreciable. But to be doubly certain, I observed the time which drops of water of known weight and area, placed on the warm calorimeter, took to dry. From these experiments it was evident that it would require a considerable area of wet surface to produce an appreciable effect. This wet surface never existed unless the calorimeter was wet by dew deposited on the cool surface. To guard against this error, the calorimeter was never cooled so low that dew formed; it was carefully rubbed with a towel, and placed in the apparatus half an hour to an hour before the experiment, exposed freely to the air. The surface being polished, the slightest deposit of dew was readily visible. The greatest care was taken to guard against this source of error, and I think the experiment is free from it.

#### (d.) Results.

##### 1. CONSTANT DATA.

Joule's equivalent in gravitation measure is of the dimensions of length only, being the height which water would have to fall to be heated one degree. Or let water flow downward with uniform velocity through a capillary tube impervious to heat; assuming the viscosity constant, the rate of variation of height with temperature will be Joule's equivalent.

Hence, besides the force of gravity the only thing required in ab-

solute measure is some length. The length that enters the equation is the diameter of the torsion wheel. This was determined under a microscope comparator by comparison with a standard meter belonging to Professor Rogers of Harvard Observatory, which had been compared at Washington with the Coast Survey standards, as well as by comparison with one of our own meter scales which had also been so compared. The result was .26908 meter at 20° C.

To this must be added the thickness of the silk tape suspending the weights. This thickness was carefully determined by a micrometer screw while the tape was stretched, the screw having a flat end. The result was .00031<sup>m</sup>.

So that, finally,  $D = .26939$  meter at 20° C. Separating the constant from the variable parts, the formula now becomes

$$\frac{J}{g} = \frac{86.324}{A + .347} \left( 1 + .000018 (t'' - 20) + \frac{.0006}{W} - .835 \lambda \right) \frac{W_n}{t - t''}.$$

$$g = 9.8005 \text{ at Baltimore.}$$

It is unnecessary to have the weights exact to standard, provided they are relatively correct, or to make double weighings, provided the same scale of the balance is always used. For both numerator and denominator of the fraction contain a weight.

## 2. EXPERIMENTAL DATA AND TABLES OF RESULTS.

In exhibiting the results of the experiments, it is much more satisfactory to compute at once from the observations the work necessary to raise 1<sup>kg</sup> of the water from the first temperature observed to each succeeding temperature. By interpolation in such a table we can then reduce to even degrees. To compare the different results I have then added to each table such a quantity as to bring the result at 20° about equal to 10,000 kilogramme meters.

The process for each experiment may be described as follows. The calorimeter was first filled with distilled water a little cooler than the atmosphere, but not so cool as to cause a deposit of dew. It was then placed in the machine and adjusted to its position, though the outer half of the jacket was left off for some time, so that the calorimeter should become perfectly dry; to aid which the calorimeter was polished with a cloth. The thermometer and safety-tube were also inserted at this time.

After half an hour or so, the chronograph was adjusted, the outer half of the jacket put in place, the wooden screen fixed in position, and all was ready to start. The engine, which had been running

quietly for some time, was now attached, and the experiment commenced. First the weights had to be adjusted so as to produce equilibrium as nearly as possible.

The observers then took their positions. One observer constantly recorded the transit of the mercury over the divisions of the thermometer, making other suitable marks, so that the divisions could be afterwards recognized. He also read the thermometers giving the temperatures of the air, the bottom of the calorimeter thermometer, and of the wheel just above the calorimeter; and sometimes another, giving that of the cast-iron frame of the instrument.

The other observer read the torsion wheel once every revolution of the chronograph cylinder, recording the time by his watch. He also recorded on the chronograph every five minutes by his watch, and likewise stirred the water in the jacket at intervals, and read its temperature.

The recording of the time was for the purpose of giving the connecting link between the readings of the torsion circle and of the thermometer. This, however, as the readings were quite constant, had only to be done roughly, say to half a minute of time, though the records of time on the chronograph were true to about a second.

The thermometers to read the temperature of the water in the jacket were graduated to  $0^{\circ}.2$  C., but were generally read to  $0^{\circ}.1$  C., and had been compared with the standards. There was no object in using more delicate thermometers.

After the experiment had continued long enough, the engine was stopped and a radiation experiment begun. The last operation was to weigh the calorimeter again, after removing the thermometer and safety-tube, and also the weights which had been used.

The chronograph sheet, having then been removed from the cylinder, had the time records identified and marked, as well as the thermometer records. Each line of the chronograph record was then numbered arbitrarily, and a table made indicating the stand of the thermometer and the number of the revolutions and fractions of a revolution as recorded on the chronograph sheet. The times at which these temperatures were reached was also found by interpolation, and recorded in another column.

From the column of times the readings of the torsion circle could be identified, and so all the necessary data would be at hand for calculating the work required to raise the temperature of one kilogramme of the water from the first recorded temperature to any succeeding temperature.

As these temperatures usually contained fractions, the amount of work necessary to raise one kilogramme of the water to the even degrees could then be found from this table by interpolation. Joule's equivalent at any point would then be merely the difference of any two succeeding numbers; or, better, one tenth the difference of two numbers situated  $10^\circ$  apart, or, in general, the difference of the numbers divided by the difference of the temperatures.

It would be a perfectly simple matter to make the record of the torsion circle entirely automatic, and I think I shall modify the apparatus in that manner in the future.

It would take too much space to give the details of each experiment; but, to show the process of calculation, I will give the experiment of Dec. 17, 1878 as a specimen. The chronograph sheet, of course, I cannot give. The computation is at first in gravitation measure, but afterwards reduced to absolute measure.

The calorimeter before the experiment weighed 12.2733 kil.

"	"	after	"	"	"	12.2716	"
					Mean	12.2720	"
					Weight of calorimeter alone	3.8721	"
					∴ Water alone weighed	8.3999	"
						.3470	"
					Total capacity	8.7469	"

The correction for weighing in air was  $.835 \lambda = .00106$ .

The total term containing the correction is therefore .99878.

$$\begin{array}{rcl}
 \log 86.324 & = & 1.9361316 \\
 \log .99878 & = & 1.9994698 \\
 & & \hline
 & & 1.9356014 \\
 \log 8.7469 & = & .9418542 \\
 \log \text{ const. factor} & = & .9987472 = \log 9.85706.
 \end{array}$$

Hence the work per kilogramme is  $9.85706 \Sigma Wn$  in gravitation measure, the term  $\Sigma Wn$  being used to denote the sum of products similar to  $Wn$  as obtained by simultaneous readings of torsion circle and records on chronograph sheet.

Zero of torsion wheel,  $79.3^{\text{mm}}$ .

Value of  $1^{\text{mm}}$  on torsion wheel  $.0118^{\text{kl}}$ .

The following were the records of time on the chronograph sheet:—

Time observed.	Revolutions of Chronograph.	Time calculated.
15	8.74	15.2
20	25.32	20.1
25	42.10	25.0
30	59.05	30.0
35	76.00	35.0
40	93.03	40.0
45	109.97	45.0
50	126.92	50.0
55	144.14	55.0

The times were calculated by the formula

$$\text{Time} = .294 \times \text{Revolutions} + 12.66,$$

which assumes that the engine moves with uniform velocity. As the principal error in using an incorrect interpolation formula comes from the calculation of the radiation, and as this formula is correct within a few seconds for all the higher temperatures, we can use it in the calculation of the times.

The records of the transits of the mercury over the divisions of the thermometer were nearly always made for each division, but it is useless to calculate for each. I usually select the even centimeters, and take the mean of the records for several divisions on each side.

While the mercury was rising  $1^{\text{cm}}$  on No. 6163, there would be about seven revolutions of the chronograph, and consequently seven readings of the torsion circle, each one of which was the average for a little time as estimated by the eye.

I have obtained more than thirty series of results, but have thus far reduced only fourteen, five of which are preliminary, or were made with the simple jacket instead of the water jacket, the radiation to which was much greater, as there was a hole at the bottom which allowed more circulation of the air. The mean of the preliminary results agrees so closely with the mean of the final results, that I have in the end given them equal weight.

On March 24th, the same thermometer was used for a second experiment directly after the first, seeing that the chronograph failed to work in the first experiment until  $8^{\circ}$  was reached. The error from this cause was small, as the first experiment only reached to  $26^{\circ}$  C., and hence there could have been no change of zero, as this is very nearly the temperature at which the thermometer was generally kept.

Having thus calculated the work in conjunction with the temperature, I have next interpolated so as to obtain the work at the even

degrees. The tables so formed I have combined in two ways: first, I have added to the column of work in each table an arbitrary number, such as to make the work at  $20^{\circ}$  about 10,000, and have then combined them as seen in Table LI.; and, secondly, I have subtracted each number from the one  $10^{\circ}$  farther down the table, and divided the numbers so found by 10, thus obtaining the mechanical equivalent of heat.

In these tables four thermometers have been used, and yet they were so accurate that little difference can be observed in the experiments which can be traced to an error of the thermometer, although the Kew standard has some local irregularities. The *greatest* difference between any column of Table LI. and the general mean is only 10 kilogramme-meters, or 0.023 degree, and this includes all errors of calibration of thermometers, radiation, &c. This seems to me to be a very remarkable result, and demonstrates the surpassing accuracy of the method. Indeed, the limit of accuracy in thermometry is the only limit which we can at present give to this method of experiment. Hence the large proportional time spent on that subject.

The accuracy of the radiation is demonstrated, to some extent, by the agreement of the results obtained even with different temperatures of the jacket. But on close observation it seems apparent that the coefficients of radiation should be further increased as there is a tendency of the end figures in each series to become too high. This is exactly what we should suppose, as we have seen that nearly all sources of error tend in the direction of making the radiation too small. For instance, an error came from not stirring the water during the radiation, and there must be a small residual error from not stirring so fast during radiation as during the experiment. Besides this, some parts around the calorimeter were warm during the radiation which were cool during the experiment. And both of these make the correction for radiation too small. However, the error from this source is small, and cannot possibly affect the general conclusions. In each column of Tables LI. and LII. a dash is placed at the temperature of the jacket, and for fifteen degrees below this point the error in the radiation must produce only an inappreciable error in the equivalent: taking the observations within this limit as the standards, and rejecting the others, we should still arrive at very nearly the same conclusions as if we accepted the whole.

Most of the experiments are made with a weight of about  $7.3^{\text{kil.}}$  as everything seemed to work best with this weight. But for the sake of a test I have run the weight up to 8.6 and down to  $4.4^{\text{kil.}}$  by which the rate of generation of the heat was changed nearly three times.

By this the correction for the radiation and the error due to the irregularity of the engine are changed, and yet scarcely an appreciable difference in the results can be observed.

The tables explain themselves very well, but some remarks may be in order. Tables XXXVII. to L. inclusive are the results of fourteen experiments selected from the total of about thirty, the others not having been worked up yet, though I propose to do so at my leisure.

Table LI. gives the collected results. At the top of each column the date of the experiment and number of the thermometer are given, together with the approximate torsion weight and the rate of rise of temperature per hour. The dash in each column gives approximately the temperature of the jacket, and hence of the air. There are four columns of mean values, but the last, produced from the combination of the table by parts, is the best.

Table LII. gives the mechanical equivalent of heat as deduced from intervals of  $10^{\circ}$  on Table LI. The selection of intervals of  $10^{\circ}$  tends to screen the variation of the specific heat of water from view, but a smaller interval gives too many local irregularities. In taking the mean I have given all the observations equal weight, but as the Kew standard was only graduated to  $\frac{1}{2}^{\circ}$  F. it was impossible to calibrate it so accurately as to avoid irregularities of  $0^{\circ}.02$  C. which would affect the quantities 1 in 500. Hence, in drawing a curve through the results, as given in the last column, I have almost neglected the Kew, and have otherwise sought to draw a regular curve without points of inflection. The figures in the last column I consider the best.

Table LIII. takes the mean values as found in Tables LI. and LII., and exhibits them with respect to the temperatures on the different thermometers, to the different parts of the earth, and also gives the reduction to the absolute scale. I am inclined to favor the absolute scale, using  $m = .00015$ , as given in the Appendix to Thermometry, rather than  $.00018$ , as used throughout the paper.

Table LIV. gives what I consider the final result of the experiment. It is based on the result  $m = .00015$  for the thermometers, and is corrected for the irregularity of the engine by adding 1 in 4000.

The minor irregularities are also corrected so that the results signify a smooth curve, without irregularity or points of contrary flexure. But the curve for the work does not differ more than three kilogramme-meters from the actual experiment at any point, and generally coincides with it to about one kilogramme-meter. These differences signify  $0^{\circ}.007$  C. and  $0^{\circ}.002$  C., respectively. The mechanical equivalent is for single degrees rather than for ten degrees, as in the other tables.

TABLE XXXVII.—FIRST SERIES.—*Preliminary.*

January 16, 1878. Jacket and Air about 14° C.

Thermometer No. 6168.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph Σ n.	Mean Weight W.	Work per Kilogramme.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 6880.
		Stem.	Rad.							
140	52.0	— .005	0	9.185	5.485	7.509	0	10	...	5728
160	58.0	— .003	— .017	11.412	18.028	7.478	951	10	348	6155
180	59.2	0	— .022	13.650	30.652	7.442	1908	11	775	6582
208	63.4	+ .006	— .015	16.230	45.329	7.394	3010	12	1202	7009
220	68.5	+ .011	— .001	18.137	56.241	7.364	3825	13	1629	7436
240	70.2	+ .020	+ .027	20.392	69.153	7.354	4786	14	2066	7864
259	74.0	+ .028	+ .067	22.538	81.484	7.292	5702	15	2484	8292
289	80.0	+ .045	+ .161	25.943	101.214	...	7156	16	2912	8720
...	...	...	...	...	...	...	...	17	3340	9147
...	...	...	...	...	...	...	...	18	3767	9578
...	...	...	...	...	...	...	...	19	4198	9999
...	...	...	...	...	...	...	...	20	4619	10428
...	...	...	...	...	...	...	...	21	5048	10852
...	...	...	...	...	...	...	...	22	5472	11279
...	...	...	...	...	...	...	...	23	5899	11706
...	...	...	...	...	...	...	...	24	6326	12133
...	...	...	...	...	...	...	...	25	6753	12560
...	...	...	...	...	...	...	...	26	7180	...

TABLE XXXVIII.—SECOND SERIES.—*Preliminary.*

March 7, 1878. Jacket 18°·5 to 22°·5. Air about 21° C.

Thermometer No. 6168.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph Σ n.	Mean Weight W.	Work per Kilogramme = Σ 10.080 W n.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 6812.
		Stem.	Rad.							
170	19.9	— .016	0	12.537	5.08	7.787	0	13	198	7010
180	...	...	...	13.646	11.12	7.710	474	14	625	7487
190	...	...	...	14.755	17.22	7.666	947	15	1052	7864
200	...	...	...	15.863	23.36	7.642	1421	16	1480	8292
210	26.8	— .010	— .036	16.972	29.55	7.641	1897	17	1909	8721
220	...	...	...	18.085	35.70	7.630	2369	18	2333	9145
230	...	...	...	19.196	41.90	7.611	2845	19	2761	9573
240	...	...	...	20.305	48.09	7.600	3319	20	3189	10001
250	33.8	+ .003	— .036	21.419	54.30	7.596	3794	21	3615	10427
260	...	...	...	22.533	...	7.582	...	22	4041	10853
270	...	...	...	23.642	66.69	7.552	4740	23	4467	11279
280	...	...	...	24.754	72.92	7.547	5213	24	4892	11704
290	40.8	+ .020	— .001	25.867	79.16	7.576	5687	25	5318	12130
300	...	...	...	26.990	85.42	...	6164	26	5744	12556

\* In the calculation of this column, more exact data were used than given in the other two columns, seeing that the original calculation was made every 5 mm. of the thermometer. Hence the last figure may not always agree with the rest of the data.



TABLE XXXVIII.—*Continued.*

Thermometer No. 6163.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph Σ n.	Mean Weight W.	Work per Kilogramme = Σ 10.060 W n.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 6612.
		Stem.	Rad.							
310	...	...	...	28.119	91.67	7.611	6643	27	6168	12080
320	...	...	...	29.253	97.98	7.604	7125	28	6598	18405
330	47.8	+0.04	+0.078	30.398	104.28	7.611	7608	29	7017	18829
340	...	...	...	31.540	110.87	7.617	8097	30	7441	14268
350	51.4	...	...	32.689	117.12	7.602	8590	31	7867	14079
360	...	...	...	33.842	123.54	7.592	9081	32	8294	16108
370	55.0	+0.072	+0.184	34.998	130.04	7.576	9576	33	8722	15584
380	...	...	...	36.168	136.56	7.550	10071	34	9149	15981
390	58.7	+0.588	+0.201	37.821	143.08	7.550	10567	35	9577	16389
...	...	...	...	...	...	...	...	36	10004	16816
...	...	...	...	...	...	...	...	37	10480	17242

TABLE XXXIX.—THIRD SERIES.—*Preliminary.*

March 12, 1878. Jacket 13°.2 to 16°.6. Air about 15° C.

Thermometer No. 6163.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph Σ n.	* Mean Weight W.	Work per Kilogramme = Σ 9.9690 W n.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 7690.
		Stem.	Rad.							
205	28.0	0	0	14.868	8.156	7.5167	0	°	....	....
210	28.6	0	+0.002	14.764	5.834		184	15	269	7868
220	29.9	...	...	15.529	9.770		495	10	690	8295
230	31.1	+0.008	+0.010	16.307	14.184	7.5462	827	17	1122	8721
240	32.4	...	...	17.090	18.642		1160	18	1548	9147
250	33.6	+0.009	+0.021	17.875	23.080		1495	19	1975	9574
260	34.9	...	...	18.662	27.550	7.5668	1881	20	2401	10000
270	36.2	+0.014	+0.038	19.452	32.014		2167	21	2828	10427
280	37.4	...	...	20.242	36.474		2504	22	3253	10852
290	38.7	+0.019	+0.055	21.029	40.924	7.5875	2840	23	3676	11275
300	39.9	...	...	21.825	45.424		3179	24	4101	11700
310	41.2	+0.024	+0.089	22.619	49.838		3514	25	4526	12125
320	42.5	...	...	23.418	54.302	7.5768	3853	26	4951	12550
330	43.7	+0.030	+0.120	24.220	58.844		4194	27	5378	12977
340	45.0	...	...	25.028	63.366		4536	28	5803	13402
350	46.3	+0.038	+0.159	25.825	67.874	7.5872	4876	29	6226	13825
360	47.6	...	...	26.628	72.408		5219	30	6653	14252
370	48.9	+0.047	+0.202	27.438	76.987		5565	31	7078	14677
380	50.1	...	...	28.253	81.550	7.5801	5910	...	...	...
390	51.4	+0.056	+0.251	29.069	86.100		6255	...	...	...
400	52.7	...	...	29.884	90.720		6604	...	...	...
410	54.0	+0.066	+0.304	30.708	95.316	....	6951	...	...	...
420	55.8	...	...	31.519	99.920		7299	...	...	...

\* As this table was originally calculated for every 5 mm. on the thermometer, I have given the weights which were used to check the more exact calculation.

TABLE XL. — FOURTH SERIES. — *Preliminary.\**

March 24, 1878. Jacket 5°.4 to 8°.2. Air about 6° C.

Thermometer No. 6168.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph Σ n.	Mean Weight W.	Work per Kilogramme = Σ 9.8616 W n.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 4902.
		Stem.	Rad.							
130	27.4	+ .002	0	8.071	42.364	7.471	0	8	— 80	4872
140	29.2	....	....	9.204	48.898	7.446	485	9	398	5300
150	31.0	+ .010	+ .019	10.840	55.438	7.442	908	10	823	5725
160	32.9	....	....	11.480	62.066	7.405	1458	11	1252	6154
170	34.7	+ .017	+ .050	12.620	68.669	7.390	1944	12	1680	6582
180	36.6	....	....	13.763	75.330	7.398	2433	13	2107	7009
190	38.4	+ .025	+ .093	14.908	81.973	7.481	2921	14	2531	7436
200	40.3	....	....	16.064	88.507	7.429	3410	15	3000	8862
210	42.2	+ .034	+ .150	17.202	95.264	7.437	3902	16	3387	9289
220	44.2	....	....	18.350	101.941	7.437	4395	17	3815	9717
230	46.1	+ .046	+ .222	19.504	108.588	7.433	4886	18	4245	9147
240	....	....	....	....	....	7.4617	....	19	4672	9574
250	....	....	....	....	....		....	20	5098	10000
260	....	....	....	....	....		....	21	5524	10426
270	53.6	+ .073	+ .399	24.124	185.158	7.509	6855	22	5960	10852
280	55.7	....	....	25.288	141.803	7.502	7350	23	6376	11278
290	57.7	+ .084	+ .524	26.466	148.427	....	7844	24	6802	11704
....	....	....	....	....	....	....	....	25	7228	12180
....	....	....	....	....	....	....	....	26	7651	12553

TABLE XLI. — FIFTH SERIES. — *Preliminary.*

March 24, 1878. Jacket 5°.4 to 8°.4. Air about 6° C.

Thermometer No. 6168.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph Σ n.	Mean Weight W.	Work per Kilogramme = Σ 9.8616 W n.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 2260.
		Stem.	Rad.							
75	0.9	— .003	0	1.891	8.154	8.1544	0	2	46	2296
80	1.7	....	....	2.451	6.118	8.0900	239	3	477	2727
90	3.4	— .002	— .012	3.569	12.174	8.0409	723	4	906	3156
100	5.1	....	....	4.690	18.172	8.0074	1200	5	1332	3582
110	6.8	0	— .017	5.810	24.212	7.9170	1677	6	1759	4009
120	8.5	....	....	6.936	30.397	7.8978	2161	7	2189	4439
130	10.2	+ .003	— .012	8.060	36.621	7.8786	2647	8	2621	4871
140	12.0	....	....	9.190	42.864	7.8512	3132	9	3050	5300
150	13.7	+ .007	+ .005	10.323	49.068	7.8061	3614	10	3477	5727
160	15.5	....	....	11.459	55.398	7.7799	4103	11	3905	6155
170	17.2	+ .015	+ .032	12.600	61.707	7.7622	4588	12	4333	6583
180	19.0	....	....	13.742	68.086	7.7643	5073	13	4759	7009
190	20.8	+ .024	+ .068	14.882	74.358	7.7807	5558	14	5183	7433
200	22.6	+ .028	+ .092	16.025	80.716	7.8419	6047	15	5608	7858
210	24.3	....	....	17.170	87.064	7.8468	6539	16	6036	8286
220	26.1	+ .039	+ .150	18.316	93.402	7.8579	7030	17	6466	8716
230	27.9	....	....	19.467	99.677	....	7518	18	6896	9145

\* The first part of the experiments were lost, as the pen of the chronograph did not work.

TABLE XLII.—Continued.

Thermometer No. 6183.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph $\times$ n.	Mean Weight W.	Work per Kilogramme = $\times 9.8318$ W n.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 2860.
		Stem.	Rad.							
240	29.6	+ .050	+ .270	20.615	105.950	7.8802	8006	19	7820	9670
250	...	...	...	...	...	7.8980	...	20	7745	9995
260	...	...	...	...	...	...	...	21	8170	10420
270	34.9	+ .080	+ .351	24.072	124.868	7.9038	9482	22	8597	10847
280	36.7	...	...	25.231	181.181	7.9091	9976	23	9024	11274
290	38.5	+ .087	+ .450	26.895	187.560	7.8979	10474	24	9451	11701
300	40.2	...	...	27.565	148.972	7.8974	10974	25	9878	11128
310	42.1	+ .109	+ .588	28.748	150.467	...	11481	26	10305	12555
...	...	...	...	...	...	...	...	27	10783	12983
...	...	...	...	...	...	...	...	28	11160	13410

TABLE XLII.—SIXTH SERIES.

May 14, 1878. Jacket 12°.1 to 12°.4. Air about 13° C.

Thermometer No. 6165.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph $\times$ n.	Mean Weight W.	Work per Kilogramme = $\times 9.8031$ W n.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 5435.
		Stem.	Rad.							
140	46.4	— .002	0	9.819	1.98	7.2291	0	9	—187	5296
150	47.9	...	...	10.178	7.07	...	370	10	293	5726
160	49.4	— .000	— .007	11.032	12.19	7.1608	735	11	721	6154
170	50.9	...	...	11.886	17.87	...	1102	12	1151	6584
180	52.5	+ .002	— .008	12.740	22.52	7.1500	1467	13	1579	7012
190	54.0	...	...	13.596	27.70	...	1835	14	2007	7440
200	55.5	+ .006	— .002	14.454	32.88	7.1512	2201	15	2434	7867
210	57.0	...	...	15.314	38.07	...	2568	16	2863	8296
220	58.5	+ .010	+ .011	16.174	43.29	7.1446	2938	17	3290	8723
230	60.0	...	...	17.037	48.50	...	3306	18	3716	9149
240	61.6	+ .015	+ .031	17.093	53.70	7.1586	3675	19	4142	9575
250	...	...	...	...	...	...	...	20	4567	10000
260	...	...	...	...	...	7.1230	...	21	4993	10426
270	66.2	+ .024	+ .075	20.500	69.27	...	4778	22	5420	10853
280	67.7	...	...	21.362	74.50	7.1344	5148	23	5846	11279
290	69.2	+ .031	+ .118	22.220	79.69	...	5514	24	6271	11704
300	70.7	...	...	23.076	84.84	7.1802	5878	25	6696	12129
310	72.2	+ .039	+ .158	23.928	89.97	...	6240	26	7121	12554
320	73.7	...	...	24.774	95.05	7.1117	6600	27	7547	12980
330	75.2	+ .047	+ .212	25.624	100.19	...	6962	28	7973	13406
340	76.2	...	...	26.467	105.27	7.0958	7319	29	8400	13833
350	78.2	+ .056	+ .272	27.309	110.39	...	7680	30	8829	14262
360	79.7	...	...	28.147	115.44	7.1076	8035	31	9259	14692
370	81.2	+ .065	+ .341	28.990	120.57	...	8396	32	9678	15111
380	82.7	...	...	29.825	125.66	7.1088	8754	33	10098	15529
390	84.2	+ .076	+ .417	30.668	130.78	...	9115	...	...	...
400	85.7	...	...	31.505	135.90	7.1064	9475	...	...	...
410	87.2	+ .087	+ .504	32.377	140.98	...	9833	...	...	...
420	88.7	...	...	33.220	146.08	...	10192	...	...	...

TABLE XLIII.—SEVENTH SERIES.

May 15, 1878. Jacket 11°·8 to 12°. Air about 12° C.

Thermometer No. 6163.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph × n.	Mean Weight W.	Work per Kilogramme = 2·93837 W n.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 5097.
		Stem.	Rad.							
130	30.9	—·004	0	8.538	5.07		0	°	....	....
140	32.2	....	....	9.815	9.73	7.2250	335	9	199	5206
150	33.6	—·002	—·006	10.094	14.86		668	10	628	5726
160	35.0	....	....	10.875	18.98	7.3011	1008	11	1056	6153
170	36.3	0	—·010	11.654	28.66		1335	12	1484	6581
180	37.6	....	....	12.438	28.16	7.3165	1670	13	1918	7010
190	38.9	+·003	—·008	13.209	32.74		2008	14	2344	7441
200	40.2	....	....	13.984	37.81	7.3460	2337	15	2770	7867
210	41.5	+·006	—·000	14.758	41.84		2667	16	3196	8293
220	42.8	....	....	15.536	46.38	7.3094	2998	17	3623	8720
230	44.2	+·010	+·013	16.317	50.99		3332	18	4052	9149
240	45.5	....	....	17.103	55.62	7.2846	3667	19	4478	9575
250	46.9	+·014	+·032	17.891	60.29		4005	20	4906	10008
260	48.3	....	....	18.682	....	7.2822	....	21	5324	10421
270	49.6	+·019	+·056	19.475	69.63		4681	22	5754	10851
280	50.9	....	....	20.269	74.84	7.2610	5021	23	6179	11276
290	52.3	+·025	+·090	21.079	79.01		5358	24	6603	11700
300	53.6	....	....	21.866	83.71	7.2504	5697	25	7028	12125
310	55.0	+·032	+·127	22.665	88.42		6037	26	7454	12551
320	56.4	....	....	23.471	93.14	7.2893	6379	27	7883	12980
330	57.8	+·039	+·172	24.281	97.88		6722	28	8307	13404
340	59.2	....	....	25.088	102.61	7.3047	7065	29	8729	13826
350	60.5	+·046	+·222	25.896	107.36		7410	30	9157	14254
360	61.9	....	....	26.706	112.14	7.3389	7759	31	9582	14679
370	63.2	+·065	+·279	27.523	116.88		8104	32	10009	15106
380	64.6	....	....	28.346	121.62	7.4109	8454	....	....	....
390	66.0	+·065	+·315	29.172	126.34		8801	....	....	....
400	67.4	....	....	29.996	131.12	7.4856	9155	....	....	....
410	68.8	+·075	+·419	30.827	135.90		9508	....	....	....
420	70.1	+·080	+·456	31.653	140.66	7.4581	9861	....	....	....

TABLE XLIV.—EIGHTH SERIES.

May 23, 1878. Jacket 16°·2 to 16°·5. Air about 20° C.

Thermometer No. 6166.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph × n.	Mean Weight W.	Work per Kilogramme = 2·93075 W n.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 8469.
		Stem.	Rad.							
230	23.9	—·007	0	16.287	39.120	6.9137	0	°	....	....
240	25.4	....	....	17.063	43.982		333	17	306	8715
250	26.8	....	....	....	....	6.9358	....	18	735	9144
260	28.3	....	....	....	....		....	19	1103	9572
270	29.7	—·000	+·005	19.405	58.602	6.9007	1338	20	1592	10001
280	31.2	....	....	20.190	63.503	6.9125	1678	21	2019	10428
290	32.7	....	....	20.975	68.428		2010	22	2446	10855

TABLE XLIV.—Continued.

Thermometer No. 6168.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph × n.	Mean Weight W.	Work per Kilogramme = 29.8075 W n.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 8406.
		Stem.	Rad.							
300	34.2	....	....	21.765	73.851	6.8878	2846	28	2871	11280
310	35.6	+ .008	+ .040	22.664	78.288	6.8866	2682	24	8208	11707
320	37.1	....	....	23.850	83.245	6.8604	3020	25	8722	12181
330	38.6	....	....	24.151	88.314	6.8358	3363	26	4160	12559
340	40.1	+ .017	+ .085	24.952	93.294	6.8748	3702	27	4574	12988
350	41.6	....	....	25.751	98.275	6.9184	4044	28	4999	14408
360	43.1	....	....	26.552	103.232	6.9444	4385	29	5423	13832
370	44.6	+ .028	+ .144	27.361	108.216	6.9291	4727	30	5851	14260
380	46.0	....	....	28.175	113.269	6.9388	5074	31	6275	14684
390	47.5	....	....	28.989	118.281	6.9385	5418	..	....	....
400	49.0	+ .039	+ .217	29.800	123.329	6.9444	5766	..	....	....
410	50.6	....	....	30.624	128.399	6.9467	6115	..	....	....
420	52.1	+ .047	+ .281	31.445	133.480	6.9314	6404	..	....	....

TABLE XLV.—NINTH SERIES.

May 27, 1878. Jacket 19°.6 to 20°. Air about 23° C.

Thermometer No. 6163.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph × n.	Mean Weight W.	Work per Kilogramme = 29.8077 W n.	Temperature.	Work per Kilogramme.	Work per Kilogramme + 8406.
		Stem.	Rad.							
200	88.0	— .015	0	15.890	6.33	8.8108	0	16	47	8293
210	89.4	....	....	17.000	11.74		478	17	478	8719
220	40.9	— .011	— .010	18.106	17.17		946	18	901	9147
230	42.3	....	....	19.219	22.62	8.7841	1419	19	1820	9572
240	43.8	— .005	— .011	20.829	28.18		1895	20	1754	10000
250	45.3	....	....	21.442	33.68		2368	21	2180	10426
260	...	+ .002	— .004	22.552	....	8.4800	....	22	2606	10852
270	...	....	....	23.659	....		....	23	8031	11277
280	49.8	+ .009	+ .012	24.771	50.55		3785	24	3457	11708
290	51.3	....	....	25.885	56.25	8.4399	4268	25	3883	12129
300	52.9	+ .019	+ .087	27.006	61.98		4737	26	4312	12558
310	54.4	....	....	28.188	67.63		5215	27	4734	12980
320	56.0	+ .029	+ .072	29.284	73.36	8.4552	5697	28	5159	13405
330	57.5	....	....	30.404	79.15		6182	29	5584	13830
340	59.1	+ .042	+ .118	31.552	84.97		6669	30	6010	14256
350	60.6	....	....	32.702	90.85	8.4015	7159	31	6435	14681
360	62.2	+ .056	+ .178	33.853	96.78		7652	32	6860	15106
370	63.8	....	....	35.011	102.66	8.4222	8143	33	7286	15532
380	65.4	+ .071	+ .242	36.170	108.59		8638	34	7714	15960
390	67.0	....	....	37.331	114.45	8.4706	9128	35	8138	16384
400	68.6	+ .088	+ .322	38.497	120.36		9626	36	8565	16811
410	70.2	....	....	39.664	126.33	8.4316	10126	37	8988	17234
420	71.8	+ .105	+ .419	40.833	132.26		10620	38	9414	17660
...	...	....	....	....	....	....	....	39	9842	18088
...	...	....	....	....	....	....	....	40	10268	18514
...	...	....	....	....	....	....	....	41	10691	18937

TABLE XLVI.—TENTH SERIES.

June 3, 1878. Jacket 18°.1 to 18°.4. Air about 20° C.

Thermometer No. 6166.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph Σ n.	Mean Weight W.	Work per Kilogramme = $\frac{29.8978}{W} n$ .	Temperature.	Work per Kilogramme.	Work per Kilogramme + 9076.
		Stem.	Rad.							
250	4.1	-.007	0	17.838	7.82		0	18	69	9145
260	7.0	....	....	18.617	....	4.8899	....	19	496	9572
270	9.9	-.003	+.004	19.401	23.19		667	20	925	10001
280	12.8	....	....	20.188	80.95	4.8919	1005	21	1850	10426
290	15.7	+.003	+.020	20.978	88.70		1841	22	1778	10854
800	18.7	....	....	21.763	46.41	4.8912	1676	23	2204	11280
810	21.6	+.008	+.037	22.551	54.21		2014	24	2627	11708
820	24.5	....	....	23.354	62.04	4.8907	2354	25	3054	12130
880	27.5	+.014	+.078	24.162	69.02		2690	26	3479	12555
840	30.5	....	....	24.970	77.92	4.8624	3041	27	3904	12980
850	33.6	+.020	+.182	25.780	85.89		3885	28	4332	13408
860	36.6	....	....	26.503	93.94	4.8542	3721	29	4852	13828
370	39.6	+.028	+.198	27.415	102.05		4081	30	5179	14255
880	42.7	....	....	28.246	110.34	4.8362	4437	31	5604	14680
890	45.8	+.036	+.281	29.079	118.49		4786	....	....	....
400	48.0	....	....	29.911	126.66	4.8978	5141	....	....	....
410	52.0	+.044	+.377	30.754	184.80		5499	....	....	....

TABLE XLVII.—ELEVENTH SERIES.

June 10, 1878. Jacket 19°.6 to 20°. Air about 25° C.

Thermometer No. 6163.	Time.	Correction.		Corrected Temperature.	Revolutions of Chronograph Σ n.	Mean Weight W.	Work per Kilogramme = $\frac{29.8404}{W} n$ .	Temperature.	Work per Kilogramme.	Work per Kilogramme + 1020.
		Stem.	Rad.							
250	...	-.002	0	21.450	8.983		0	21	-192	10428
260	...	+.002	+.006	22.562	16.087	6.7572	476	22	285	10855
270	...	....	....	....	....	6.7678	....	23	662	11282
280	...	+.010	+.029	24.789	80.281		1421	24	1087	11707
290	...	....	....	25.907	87.489	6.7749	1899	25	1511	12131
800	...	+.019	+.003	27.032	44.655		2879	26	1939	12559
810	...	....	....	28.168	51.848	6.7896	2860	27	2365	12985
820	...	+.081	+.113	29.807	59.098		3344	28	2789	13409
330	...	....	....	30.456	66.890	6.7978	3832	29	3214	13834
840	...	+.048	+.177	31.612	78.724		4323	30	3638	14258
350	...	....	....	32.774	81.153	6.8188	4817	31	4063	14683
860	...	+.058	+.257	33.939	88.462		5311	32	4488	15108
870	...	....	....	35.110	95.734	6.9165	5807	33	4913	15533
880	...	+.072	+.351	36.280	103.093		6307	34	5337	15957
890	...	....	....	37.456	110.500	6.7876	6808	35	5760	16380
400	...	+.087	+.403	38.637	118.121		7311	36	6187	16807
410	...	....	....	39.821	125.698	6.7808	7815	37	6614	17234
420	...	+.106	+.595	41.010	183.250		8321	38	7040	17660
...	...	....	....	....	....	....	....	39	7465	18085
...	...	....	....	....	....	....	....	40	7891	18511
...	...	....	....	....	....	....	....	41	8317	18937

TABLE XLVIII. — TWELFTH SERIES. EXPERIMENT OF DECEMBER 17, 1878.

Thermometer No. 6168.	Temperatures.†			Corrections.			Total.	Corrected Temperature.	Revolutions of Chronograph.	Time.	Δ Revolutions of Chronograph.	Mean Wt.	Work per Kilogramme.		Work per Kilogramme by Interpolation.	Work per Kilogramme. + 1860.
	Water.	Air.	Tube at bottom of 6168.	Radiation.	Part in Air.	Part in Tube of Water.							9.85706 Wm.	9.85706 Wm.		
70	1.248	8.6	4.8	0	0	0	0	1.248	5.22	14.2	6.84	7.213	486.3	486.3	-107	1863
80	2.380	8.27	4.8	0.005	0	0	-0.003	2.377	12.06	16.2	6.89	7.126	484.0	484.0	+824	2284
90	3.503	8.7	4.2	-0.005	0	0	-0.005	3.498	18.95	18.3	6.89	7.104	482.6	482.6	755	2715
100	4.026	8.30	4.1	+0.003	+0.002	0	-0.002	4.624	25.84	20.3	7.08	6.980	487.1	1452.8	4	3145
110	5.747	8.9	4.1	+0.003	+0.005	0	+0.005	5.752	32.92	22.4	7.00	7.080	488.5	1093.9	6	3575
120	6.808	8.30	4.0	+0.022	+0.005	0	-0.014	6.882	39.92	24.4	6.89	7.155	486.9	2428.4	7	4006
130	7.989	4.0	4.0	+0.054	+0.010	0	-0.027	8.016	46.81	26.4	6.89	7.193	488.6	2014.8	6	4439
140	9.110	3.83	4.1	+0.101	+0.017	0	-0.064	9.154	58.70	28.4	6.92	7.210	491.8	3402.8	8	4867
150	10.231	3.35	4.1	+0.161	0	0	+0.090	10.295	60.62	30.5	6.89	7.168	486.8	3894.6	9	5297
160	11.352	3.35	4.1	+0.161	0	0	-0.118	11.442	67.51	32.5	6.88	7.151	492.0	4873.4	10	5727
170	12.473	3.35	4.2	+0.160	0	0	-0.151	12.591	74.49	34.6	6.99	7.137	491.7	5865.2	11	6153
180	13.592	3.35	4.5	+0.224	+0.025	0	-0.185	13.743	81.48	36.6	6.98	7.159	492.6	5857.7	12	6580
190	14.710	3.35	4.8	+0.224	+0.025	0	-0.226	14.895	88.40	38.7	6.98	7.155	490.9	6348.5	13	7008
200	15.825	3.35	4.8	+0.224	+0.025	0	-0.287	16.051	95.44	40.7	7.00	7.155	493.7	6842.3	14	7485
210	16.938	3.40	4.8	+0.224	+0.034	0	-0.316	17.205	102.44	42.8	7.01	7.202	497.6	7389.9	15	7882
220	18.047	3.40	4.5	+0.224	+0.034	0	-0.386	18.363	109.45	44.8	6.97	7.193	494.2	7834.2	16	8287
230	19.157	3.50	5.2	+0.224	+0.034	0	-0.428	19.528	116.42	46.9	7.05	7.210	501.4	8385.2	17	8715
240	20.265	3.50	5.6	+0.224	+0.034	0	-0.481	20.688	123.47	48.9	13.96	7.207	501.7	8885.2	18	9144
250	21.372	3.50	5.6	+0.224	+0.034	0	-0.547	21.853	130.47	50.9	7.01	7.213	498.4	9326.9	19	9571
260	22.474	3.53	5.8	+0.224	+0.034	0	-0.615	23.021	137.48	53.0	7.07	7.185	500.7	9826.3	20	9999
270	23.572	3.53	5.9	+0.224	+0.034	0	-0.686	24.187	144.44	55.1	7.07	7.185	500.7	10326.3	21	10428
280	24.670	3.56	5.9	+0.224	+0.034	0	-0.757	25.356	151.51	57.1	7.07	7.185	500.7	10826.3	22	10853
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	23	11278
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	24	11705
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	25	12133

† These are interpolated from the observations.

• Correction for 0 point 0° 08 C. In the experiments previous to this, no correction was necessary.

TABLE XLIX.—THIRTEENTH SERIES.

Dec. 19, 1878. Jacket 8°2 to 8°5. Air 4°2 to 5°2 C.

Thermometer No. 8183.	Corrections.		Corrected Temperature.	Revolutions of Chronograph Σ n.	Mean Weight W.	Work per Kilogramme $9.8088 \times Wn$ .	Σ 9.8088 Wn.	Temperature.	Work per Kilogramme.	Work + 1864.
	Stem.	Rad.								
70	0	0	1.248	1.72	8.0610	485.0	0	1	-106	1858
80	....	....	2.378	7.88	8.5571	485.1	485.0	2	+323	2287
90	0	-.008	3.500	13.11	8.4325	482.2	970.1	3	754	2718
100	....	....	4.626	18.89	8.3688	481.1	1452.3	4	1184	3148
110	+.001	+.003	5.751	24.70	8.4155	487.1	1938.4	5	1612	3576
120	....	....	6.881	30.55	8.4180	485.0	2420.5	6	2041	4005
130	+.005	+.019	8.013	36.38	8.3953	489.2	2906.1	7	2472	4436
140	....	....	9.148	42.27	8.4866	486.6	3395.3	8	2901	4865
150	+.009	+.044	10.284	48.10	8.4484	486.5	3881.9	9	3331	5295
160	....	....	11.424	53.92	8.4189	490.6	4368.4	10	3760	5724
170	+.016	+.080	12.569	59.81	8.3988	491.1	4859.0	11	4187	6151
180	....	....	13.713	65.72	8.4153	487.1	5350.1	12	4615	6579
190	+.023	+.126	14.859	71.57	8.3811	491.7	5837.2	13	5045	7009
200	....	....	16.005	77.50	8.3835	489.4	6328.9	14	5472	7436
210	+.033	+.183	17.154	83.40	8.3976	490.2	6818.3	15	5898	7862
220	....	....	18.300	89.30	8.4035	493.0	7308.5	16	6327	8291
230	+.044	+.251	19.452	95.23	8.4460	496.4	7801.5	17	6753	8717
240	....	....	20.604	101.17	8.4555	981.3	8297.9	18	7180	9144
250	+.056	+.332	21.760	.....			.....	19	7608	9572
260	....	....	22.912	112.90	8.4602	494.7	9279.2	20	8038	10002
270	+.069	+.424	24.065	118.81	8.4779	494.0	9773.9	21	8465	10429
280	....	....	25.221	124.70	.....	.....	10207.9	22	8891	10855
...	....	....	.....	.....	.....	.....	.....	23	9317	11281
...	....	....	.....	.....	.....	.....	.....	24	9746	11710
...	....	....	.....	.....	.....	.....	.....	25	10173	12137



TABLE L. — FOURTEENTH SERIES.

December 20, 1878. Jacket 1°.5 to 1°.9. Air about 8°.4 C.

Temperature by Kew Standard.	Time.	Corrections.			Corrected Tem- perature, Abso- lute Scale.	Revolution of Chronograph Σ s	Mean Weight W.	Work per Kilogramme = Σ 9.7832 W s.	Temperature.	Work per Kilogramme.	Work per Kilo- gramme + 5210.
		Reduction to Absolute Scale.	Stem.	Rad.							
36.0	56.0	.00	0	0	1.82	8.03	7.8682	0	20	77	2287
38.5	58.4	....	....	....	8.23	16.87	7.8458	601	8	508	2713
41.0	.9	-.01	.00	+.01	4.62	24.78	7.8705	1206	4	936	3146
43.5	8.3	....	....	....	6.02	33.19	7.4012	1812	5	1370	3580
46.0	5.8	-.02	+.01	+.04	7.48	41.48	7.4142	2412	6	1803	4018
48.5	8.2	....	....	....	8.84	49.81	7.4177	3016	7	2226	4436
51.0	10.7	-.03	+.02	+.09	10.26	58.18	7.4390	3624	8	2656	4866
53.5	18.2	....	....	....	11.68	66.56	7.4107	4234	9	3084	5204
56.0	15.6	-.04	+.03	+.16	13.12	74.95	7.8493	4842	10	3513	5723
58.5	18.2	....	....	....	14.56	83.56	7.3269	5461	11	3942	6152
61.0	20.7	-.04	+.05	+.25	16.01	92.27	7.2335	6085	12	4360	6579
63.5	23.3	....	....	....	17.46	100.99	7.1603	6703	13	4790	7000
66.0	25.9	-.05	+.06	+.83	18.92	109.95	7.2075	7330	14	5220	7430
68.5	28.5	....	....	....	20.39	118.84	7.1839	7957	15	5650	7860
71.0	31.2	-.05	+.08	+.52	21.86	127.83	7.2122	8589	16	6081	8291
73.5	33.8	....	....	....	23.34	136.75	7.2252	9218	17	6507	8717
76.0	36.5	-.05	+.10	+.69	24.84	145.78	7.2184	9857	18	6935	9145
78.5	39.2	....	....	....	26.33	154.80	.....	10493	19	7364	9574
....	....	....	....	....	....	....	....	....	20	7791	10001
....	....	....	....	....	....	....	....	....	21	8219	10429
....	....	....	....	....	....	....	....	....	22	8648	10858
....	....	....	....	....	....	....	....	....	23	9074	11284
....	....	....	....	....	....	....	....	....	24	9499	11709
....	....	....	....	....	....	....	....	....	25	9925	12135
....	....	....	....	....	....	....	....	....	26	10352	12562

TABLE LI.—WORK IN KILOGRAMME-METERS AT BALTIMORE TO HEAT ONE KILOGRAMME OF WATER FROM AN UNKNOWN POINT TO A GIVEN TEMPERATURE ON THE ABSOLUTE SCALE.

Temperature.	Preliminary Results with simple Tin Jacket for the Radiation.					Final results with the Water Jacket around the Calorimeter to make the Radiation definite.										Mean of Preliminary Results.	Mean of Final Results.	General Results.	General Mean from Combination of Table by Parts.
	Jan. 16. 6168. Weight 7.4 kil. 86° per hour.	Mar. 7. 6168. Weight 7.6 kil. 89° per hour.	March 12. 6166. Weight 7.6 kil. 88° per hour.	March 24.		May 14. 6166. Weight 7.1 kil. 84° per hour.	May 16. 6166. Weight 6.8 kil. 86° per hour.	May 23. 6166. Weight 6.9 kil. 82° per hour.	May 27. 6168. Weight 8.6 kil. 45° per hour.	June 8. 6166. Weight 4.4 kil. 16° per hour.	June 19. 6168. Weight 6.8 kil. 81° per hour.	Dec. 17. 6168. Weight 7.2 kil. 84° per hour.	Dec. 19. 6168. Weight 8.4 kil. 48° per hour.	Dec. 20. Rev St Weight 7.3 kil. 81° per hour.					
				1 Series. 6168. Weight 7.4 kil. 86° per hour.	2 Series. 6168. Weight 7.8 kil. 89° per hour.														
2	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	2287	2287	2287	2286	2288	2289	
3	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	2713	2718	2713	2715	2718	2719	
4	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8146	8148	8146	8146	8149	8150	
5	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8575	8576	8580	.....	8578	8579	
6	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	4006	4005	4018	4008	4008	4009	
7	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	4439	4436	4436	4437	4437	4438	
8	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	4867	4865	4866	4866	4868	4868	
9	.....	.....	.....	.....	.....	.....	5296	5296	.....	.....	.....	.....	5297	5295	5294	5300	5296	5297	
10	5728	.....	.....	.....	.....	.....	5726	5725	.....	.....	.....	.....	5727	5724	5723	5727	5725	5725	
11	6155	.....	.....	.....	.....	.....	6164	6158	.....	.....	.....	.....	6153	6151	6152	6155	6153	6152	
12	6582	.....	.....	.....	.....	.....	6584	6581	.....	.....	.....	.....	6580	6579	6579	6582	6581	6580	
13	7009	7010	.....	.....	.....	.....	7012	7010	.....	.....	.....	.....	7009	7000	7000	7009	7008	7007	
14	7436	7437	.....	.....	.....	.....	7440	7441	.....	.....	.....	.....	7435	7436	7436	7438	7436	7435	
15	7864	7864	7868	7862	7858	.....	7867	7867	.....	.....	.....	.....	7862	7862	7860	7863	7864	7862	
16	8292	8292	8206	8289	8286	.....	8296	8293	.....	8213	.....	.....	8287	8291	8291	8291	8292	8291	

17	8720	8721	8721	8721	8716	8728	8720	8715	8719	.....	.....	8715	8717	8717	8719	8718	8718	8718
18	9147	9145	9147	9147	9145	9149	9140	9144	9147	9145	.....	9144	9144	9144	9146	9146	9146	9146
19	9578	9573	9574	9574	9570	9575	9575	9572	9572	9572	9572	9571	9572	9574	9573	9573	9573	9573
20	9989	10001	10000	10000	9995	10000	10003	10001	10000	10001	.....	9998	10002	10001	9999	10001	10000	10000
21	10428	10427	10427	10428	10420	10426	10421	10428	10428	10428	10428	10428	10429	10429	10426	10427	10426	10426
22	10852	10853	10852	10852	10847	10853	10851	10855	10852	10854	10855	10858	10855	10858	10851	10854	10853	10853
23	11279	11279	11275	11278	11274	11279	11276	11280	11277	11280	11282	11278	11281	11284	11277	11280	11279	11279
24	11706	11704	11700	11704	11701	11704	11700	11707	11708	11708	11707	11705	11710	11709	11708	11705	11706	11706
25	12138	12130	12125	12130	12128	12129	12125	12131	12129	12130	12131	12138	12137	12135	12120	12131	12130	12130
26	12560	12566	12560	12563	12555	12554	12551	12559	12558	12555	12559	.....	.....	12562	12555	12557	12556	12557
27	.....	12980	12977	.....	12983	12980	12980	12988	12980	12980	12985	.....	.....	.....	12980	12981	12981	12982
28	.....	18405	18402	.....	18410	18408	18404	18408	18405	18408	18409	.....	.....	.....	18406	18407	18406	18407
29	.....	13829	13825	.....	.....	13883	13826	13832	13830	13828	13834	.....	.....	.....	13827	13829	13828	13829
30	.....	14253	14252	.....	.....	14262	14254	14260	14256	14255	14258	.....	.....	.....	14253	14257	14256	14257
31	.....	14679	14677	.....	.....	14692	14679	14684	14681	14680	14683	.....	.....	.....	14678	14683	14681	14682
32	.....	15106	.....	.....	.....	15111	15106	.....	15106	.....	15108	.....	.....	.....	.....	15108	15106	15104
33	.....	15534	.....	.....	.....	15520	.....	.....	15532	.....	15538	.....	.....	.....	.....	15531	15532	15530
34	.....	15961	.....	.....	.....	.....	.....	.....	15960	.....	15957	.....	.....	.....	.....	15959	15960	15956
35	.....	16389	.....	.....	.....	.....	.....	.....	16384	.....	16380	.....	.....	.....	.....	16382	16384	16381
36	.....	16816	.....	.....	.....	.....	.....	.....	16811	.....	16807	.....	.....	.....	.....	16809	16811	16808
37	.....	17242	.....	.....	.....	.....	.....	.....	17234	.....	17234	.....	.....	.....	.....	17234	17237	17234
38	.....	.....	.....	.....	.....	.....	.....	.....	17060	.....	17060	.....	.....	.....	.....	17060	17060	17060
39	.....	.....	.....	.....	.....	.....	.....	.....	18068	.....	18056	.....	.....	.....	.....	18086	18086	18086
40	.....	.....	.....	.....	.....	.....	.....	.....	18514	.....	18511	.....	.....	.....	.....	18512	18512	18512
41	.....	.....	.....	.....	.....	.....	.....	.....	18987	.....	18987	.....	.....	.....	.....	18937	18987	18987

TABLE LIII.—MECHANICAL EQUIVALENT OF HEAT IN KILOGRAMME-METERS AT BALTIMORE, EACH VALUE CALCULATED FROM A RISE OF 10° C. IN TEMPERATURE.

Temp. C.	Jan. 16.	March 7.	March 12.	March 24.		May 14.	May 16.	May 28.	May 27.	June 8.	June 19.	Dec. 17.	Dec. 19.	Dec. 20.	General Mean.	From regu- lar Curve.
				1st Ser.	2d Ser.											
4	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
5	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	429.7
6	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	429.4
7	...	...	...	...	428.7	...	...	...	...	...	...	429.6	429.2	429.2	429.1	429.2
8	...	...	...	...	428.2	...	...	...	...	...	...	429.3	429.1	428.7	428.8	428.9
9	...	...	...	...	427.7	...	...	...	...	...	...	429.0	428.8	428.4	428.5	428.6
10	...	...	...	...	427.6	...	...	...	...	...	...	428.7	428.6	428.0	428.2	428.4
11	...	...	...	...	427.7	...	...	...	...	...	...	428.1	428.6	427.8	428.0	428.2
12	...	...	...	...	427.7	...	...	...	...	...	...	427.6	428.1	428.1	427.9	428.0
13	...	...	...	...	427.4	...	...	...	...	...	...	427.7	427.9	427.0	427.7	427.7
14	...	...	...	...	427.0	427.0	427.9	...	...	...	...	427.4	427.7	428.0	427.6	427.5
15	427.1	...	...	...	427.5	428.8	427.4	427.8	...	...	...	427.2	427.8	427.8	427.4	427.3
16	427.3	...	...	...	427.2	428.5	427.2	428.8	...	...	...	427.5	427.8	427.7	427.2	427.1
17	427.0	...	...	...	427.0	426.4	426.9	427.0	...	...	...	427.3	427.6	427.9	427.1	428.9

18	427.0	426.9	....	426.9	426.7	426.6	....	....	....	427.0	427.1	428.4	427.0	426.7
19	427.0	426.7	....	426.8	426.4	425.9	....	....	....	427.0	427.4	427.0	426.9	426.5
20	426.9	426.6	425.7	426.8	426.2	425.8	....	....	....	427.1	427.5	427.5	426.7	426.4
21	426.8	426.4	425.5	426.4	425.8	425.8	....	426.5	....	....	....	427.1	426.4	426.2
22	....	425.9	425.6	....	425.7	426.0	426.8	426.1	....	....	....	....	426.1	426.1
23	....	426.0	425.5	....	426.5	425.5	426.4	425.8	426.8	....	....	....	426.0	425.9
24	....	425.6	425.1	....	....	425.8	426.0	425.8	425.0	....	....	....	425.6	425.8
25	....	425.2	425.2	....	426.2	425.1	425.9	425.0	425.4	....	....	....	425.6	425.7
26	....	425.2	425.0	....	426.6	425.8	425.6	425.5	425.4	....	....	....	425.0	425.6
27	....	425.3	....	....	426.8	425.5	....	426.4	....	....	....	....	425.5	425.5
28	....	425.5	....	....	425.0	....	....	425.5	....	425.1	....	....	425.4	425.5
29	....	425.7	....	....	....	....	....	425.7	....	425.0	....	....	425.5	425.4
30	....	425.9	....	....	....	....	....	425.5	....	424.9	....	....	425.4	425.4
31	....	426.0	....	....	....	....	....	425.8	....	424.8	....	....	425.4	425.4
32	....	426.2	....	....	....	....	....	426.4	....	424.9	....	....	425.5	425.4
33	....	....	....	....	....	....	....	425.5	....	425.1	....	....	425.3	425.4
34	....	....	....	....	....	....	....	425.8	....	425.1	....	....	425.5	425.5
35	....	....	....	....	....	....	....	425.8	....	425.8	....	....	425.6	425.5
36	....	....	....	....	....	....	....	425.6	....	425.4	....	....	425.5	425.5

TABLE LIII.

TEMPERATURE.				WORK.				Mechanical Equivalent of Heat, 10° Series on the										
Absolute Scale.		Approximate, Mercurial Thermometer.				Per Kilogr. of Water.				Absolute Thermometric Scale.		Mercurial Thermometric Scale, the Glass similar to the						
Using $m = .00018$ .	Absolute Temp. $m = .00015$ .	Baudin 6167.	Geissler Standard.	Kew Standard.	Baudin 7316 or 7384.	Fasté.	Kilogramme-Meters at Baudin's note, B.	Kilogr.-Meters at Paris, $\frac{1}{100086}$	Kilogr.-Meters at Berlin, $\frac{1}{100117}$	Per Gramme of Water on the C. G. S. System.	Using $m = .00018$ .	Using $m = .00016$ .	Absolute C.G.S. System.	Geissler Standard.	Kew Standard.	Baudin 7316 or 7384.	Fasté.	
2	2.002	2.03	2.03	2.01	2.02	2.01	2289	2295	2298	00000.	0000.	....	....	....	....	....	....	....
3	3.003	3.04	3.04	3.01	3.02	3.01	2719	2725	2727	2443	....	....	....	....	....	....	....	....
4	4.004	4.05	4.05	4.01	4.03	4.02	3150	3156	3158	3287	....	....	....	....	....	....	....	....
5	5.005	5.06	5.07	5.02	5.04	5.02	3579	3584	3587	3707	....	....	....	....	....	....	....	....
6	6.005	6.08	6.09	6.02	6.05	6.03	4009	4014	4016	4129	....	....	....	....	....	....	....	....
7	7.006	7.09	7.10	7.02	7.05	7.03	4438	4443	4444	4549	....	....	....	....	....	....	....	....
8	8.007	8.10	8.11	8.02	8.06	8.03	4868	4872	4874	4970	....	....	....	....	....	....	....	....
9	9.007	9.11	9.12	9.02	9.07	9.04	5297	5301	5302	5391	....	....	....	....	....	....	....	....
10	10.008	10.12	10.13	10.03	10.07	10.04	5725	5729	5730	5810	....	....	....	....	....	....	....	....
11	11.008	11.13	11.14	11.03	11.08	11.04	6152	6155	6156	6229	....	....	....	....	....	....	....	....
12	12.008	12.14	12.15	12.03	12.08	12.05	6580	6583	6584	6648	....	....	....	....	....	....	....	....
13	13.009	13.15	13.16	13.04	13.09	13.05	7007	7010	7010	7067	....	....	....	....	....	....	....	....
14	14.009	14.16	14.18	14.04	14.10	14.05	7435	7437	7438	7486	....	....	....	....	....	....	....	....
15	15.009	15.17	15.18	15.04	15.10	15.05	7862	7864	7864	7905	....	....	....	....	....	....	....	....
16	16.010	16.19	16.19	16.04	16.10	16.06	8290	8291	8292	8324	....	....	....	....	....	....	....	....
17	17.010	17.20	17.21	17.04	17.11	17.06	8718	8719	8719	8744	....	....	....	....	....	....	....	....

18	18.010	18.21	18.22	18.05	18.12	18.07	9146	9147	9163	426.7	426.7	4182	4182	422.9	425.8	424.6	425.5
19	19.010	10.21	10.23	19.05	10.13	19.07	9573	9574	9582	426.5	426.5	4180	4180	422.9	425.7	424.5	425.3
20	20.010	20.22	20.23	20.05	20.13	20.07	10000	10000	10000	426.4	426.4	4179	4179	423.0	425.6	424.5	425.3
21	21.010	21.22	21.24	21.05	21.13	21.07	10426	10426	10418	426.2	426.2	4177	4177	423.0	425.5	424.4	425.1
22	22.010	22.22	22.24	22.05	22.13	22.07	10853	10852	10836	426.1	426.1	4176	4176	423.0	425.4	424.4	425.1
23	23.010	23.23	23.25	23.05	23.14	23.08	11278	11278	11253	425.9	425.9	4174	4175	423.0	425.2	424.3	424.9
24	24.010	24.23	24.25	24.06	24.14	24.08	11706	11706	11672	425.8	425.8	4173	4174	423.0	425.2	424.2	424.9
25	25.003	25.24	25.26	25.03	25.14	25.08	12128	12128	12088	425.7	425.8	4172	4173	423.1	425.1	424.2	424.8
26	26.009	26.25	26.27	26.06	26.15	26.08	12537	12554	12508	425.6	425.7	4171	4172	423.2	425.0	424.2	424.8
27	27.008	27.25	27.27	27.06	27.15	27.08	12982	12979	12922	425.5	425.5	4170	4171	423.2	425.0	424.2	424.7
28	28.008	28.25	28.27	28.06	28.15	28.08	13407	13403	13339	425.5	425.5	4170	4171	423.4	425.0	424.8	424.8
29	29.008	29.26	29.29	29.03	29.16	29.09	13829	13825	13753	425.4	425.6	4169	4171	423.4	424.9	424.3	424.7
30	30.007	30.26	30.29	30.06	30.16	30.09	14257	14252	14172	425.4	425.4	4169	4171	423.6	425.0	424.4	424.8
31	31.007	31.27	31.30	31.06	31.16	31.09	14682	14678	14588	425.4	425.6	4169	4171	423.7	425.0	424.5	424.8
32	32.005	32.27	32.30	32.06	32.16	32.09	15104	15100	15098	425.4	425.6	4169	4171	423.9	425.0	424.5	424.9
33	33.005	33.28	33.31	33.07	33.17	33.09	15530	15526	15420	425.4	425.7	4170	4172	424.0	425.1	424.6	424.9
34	34.005	34.28	34.31	34.07	34.17	34.09	15956	15951	15849	425.5	425.7	4170	4172	424.2	425.2	424.8	425.1
35	35.004	35.28	35.31	35.07	35.17	35.09	16381	16376	16264	425.5	425.8	4170	4173	424.4	425.2	424.9	425.1
36	36.003	36.29	36.32	36.07	36.17	36.10	16808	16802	16672	425.5	425.8	4170	4173	424.5	425.3	425.0	425.2
37	37.003	37.29	37.32	37.07	37.17	37.10	17284	17228	17090	....	....	....	....	....	....	....	....
38	38.002	38.29	38.32	38.07	38.17	38.10	17661	17654	17508	....	....	....	....	....	....	....	....
39	39.001	39.29	39.32	39.07	39.17	39.10	18086	18079	17925	....	....	....	....	....	....	....	....
40	40.000	40.29	40.32	40.07	40.17	40.10	18512	18505	18342	....	....	....	....	....	....	....	....
41	40.990	41.30	41.33	41.07	41.18	41.10	18937	18929	18759	....	....	....	....	....	....	....	....

\* See Appendix to Thermometry.

TABLE LIV.—FINAL MOST PROBABLE RESULTS.

Temperature on the Absolute Scale. $m = .0015$ .	Work.		Mechanical Equivalent.		Temperature on the Absolute Scale. $m = .0015$ .	Work.		Mechanical Equivalent.	
	Kilogramme-Meters at Baltimore.	Absolute C. G. S. System.	Kilogramme-Meters at Baltimore.	1° Series, Absolute C. G. S. System.		Kilogramme-Meters at Baltimore.	Absolute C. G. S. System.	Kilogramme-Meters at Baltimore.	1° Series, Absolute C. G. S. System.
20	2289	00000.	....	0000.	22	10859	00000.	....	0000.
3	2720	2443	....	....	23	11278	10835	426.1	4176
4	8150	2865	....	....	24	11704	11253	426.0	4175
5	3680	3286	....	....	25	12130	11670	425.9	4174
6	4009	8708	429.8	4212	26	12556	12088	425.8	4173
7	4439	4129	429.5	4209	27	12982	12505	425.7	4172
8	4808	4550	429.3	4207	28	13407	12922	425.6	4171
9	5297	4970	429.0	4204	29	13839	13339	425.6	4171
10	5720	5390	428.8	4202	30	14258	13833	425.5	4170
11	6154	5811	428.5	4200	31	14684	14258	425.6	4171
12	6582	6230	428.3	4198	32	15110	14684	425.6	4171
13	7010	6650	428.1	4196	33	15535	15110	425.6	4171
14	7438	7070	427.9	4194	34	15961	15535	425.7	4172
15	7865	7489	427.7	4192	35	16387	15961	425.7	4172
16	8298	7908	427.4	4189	36	16812	16387	425.8	4173
17	8720	8327	427.2	4187	37	17238	16812	425.8	4173
18	9147	8745	427.0	4185	38	17664	17238	....	....
19	9574	9164	426.8	4183	39	18091	17664	....	....
20	10000	9582	426.6	4181	40	18517	18091	....	....
21	10426	10000	426.4	4179	41	18943	18517	....	....
		10418	426.2	4177			18943	....	....

TABLE LV.—QUANTITY TO ADD TO THE EQUIVALENT AT BALTIMORE TO REDUCE TO ANY LATITUDE.

Latitude.	Addition in Kilogramme-Meters.
0	+ 0.89
10	+ 0.82
20	+ 0.68
30	+ 0.54
40	+ 0.08
50	— 0.41
60	— 0.77
70	— 1.06
80	— 1.26
90	— 1.38

Manchester —0.5; Paris —0.4; Berlin —0.5.



## V. CONCLUDING REMARKS. AND CRITICISM OF RESULTS AND METHODS.

On looking over the last four columns of Table LIII., which gives the results of the experiments as expressed in terms of the different mercurial thermometers, we cannot but be impressed with the unsatisfactory state of the science of thermometry at the present day, when nearly all physicists accept the mercurial thermometer as the standard between  $0^{\circ}$  and  $100^{\circ}$ . The wide discrepancy in the results of calorimetric experiments requires no further explanation, especially when physicists have taken no precaution with respect to the change of zero after the heating of the thermometer. They show that thermometry is an immensely difficult subject, and that the results of all physicists who have not made a special study of their thermometers, and a comparison with the air thermometer, must be greatly in error, and should be rejected in many cases. And this is specially the case where Geissler thermometers have been used.

The comparison of my own thermometers with the air thermometer is undoubtedly by far the best so far made, and I have no improvements to offer beyond those I have already mentioned in the "Appendix to Thermometry." And I now believe that, with the improvement to the air thermometer of an artificial atmosphere of constant pressure, we could be reasonably certain of obtaining the temperature at any point up to  $50^{\circ}$  C. within  $0.001$  C. from the mean of two or three observations. I believe that my own thermometers scarcely differ much more than that from the absolute scale at any point up to  $40^{\circ}$  C., but they represent the mean of eight observations. However, there is an uncertainty of  $0.001$  C. at the  $20^{\circ}$  point, owing to the uncertainty of the value of  $m$ . But taking  $m = .00015$ , I hardly think that the point is uncertain to more than that amount for the thermometers Nos. 6163, 6165, and 6166.

As to the comparison of the other thermometers, it is evidently unsatisfactory, as they do not read accurately enough. However, the figures given in Table LIII. are probably very nearly correct.

The study of the thermometers from the different makers introduces the question whether there are *any* thermometers which stand below the air thermometer between 0 and  $100^{\circ}$ . As far as I can find, nobody has ever published a table showing such a result, although Boscha *infers* that thermometers of "Cristal de Choisy-le-Roi" *should* stand below, and his inference has been accepted by Regnault. But it does not seem to have been proved by direct experiment. My

Baudin thermometers seem to contain lead as far as one can tell from the blackening in a gas flame, but they stand very much above the air thermometer at  $40^{\circ}$ . I have since tried some of the Baudin thermometers up to  $300^{\circ}$ , and find that they stand *below* the air thermometer between  $100^{\circ}$  and  $240^{\circ}$ ; they coincide at *about*  $240^{\circ}$ , and stand above between  $240^{\circ}$  and  $300^{\circ}$ . This is very nearly what Regnault found for "Verre Ordinaire." It is to be noted that the formula obtained from experiments below  $100^{\circ}$  makes them coincide at  $233^{\circ}$ , which is remarkably close to the result of actual experiment, especially as it would require a long series of experiments to determine the point within  $10^{\circ}$ .

The comparison of thermometers also shows that all thermometers in accurate investigations should be used as thermometers with arbitrary scales, neither the position of the zero point nor the interval between the  $0^{\circ}$  and  $100^{\circ}$  points being assumed correct. The text books only give the correction for the zero point, but my observations show that the interval between the  $0^{\circ}$  and  $100^{\circ}$  points is also subject to a secular change as well as to the temporary change due to heating. Of all the thermometers used, the Geissler is the worst in this as in other respects, except accuracy of calibration, in which it is equal to most of the others.

The experiments on the specific heat of water show an undoubted *decrease* as the temperature rises, a fact which will undoubtedly surprise most physicists as much as it surprised me. Indeed, the discovery of this fact put back the completion of this paper many months, as I wished to make certain of it. There is now no doubt in my mind, and I put the fact forth as proved. The only way in which an error accounting for this decrease could have been made appears to me to be in the determination of  $m$  in "Thermometry." The determination of  $m$  rests upon the determination of a difference of only  $0.05^{\circ}$  C. between the air thermometer and the mercurial, the  $0^{\circ}$  and  $40^{\circ}$  points coinciding, and also upon the comparison of the thermometers with others whose value of  $m$  was known, as in the Appendix. Although the quantity to be measured is small, yet there can be no doubt at least that  $m$  is larger than zero; and if so, the specific heat of water certainly has a minimum at about  $30^{\circ}$ .

One point that might be made against the fact is that the Kew standard, Table L., gives less change than the others. But the calibration of the Kew standard, although excellent, could hardly be trusted to  $0.02$  or  $0.03^{\circ}$  C., as the graduation was only to  $\frac{1}{2}^{\circ}$  F. In drawing the curve for the difference between the Kew standard and

the air thermometers, I ignored small irregularities and drew a regular curve. On looking over the observations again, I see that, had I taken account of the small irregularities, it would have made the observations agree more nearly with the other thermometers. Hence the objection vanishes. However, I intend working up some observations which I have with the Kew standard at a higher temperature, and shall publish them at a future time.

There is one other error that might produce an apparent decrease in the specific heat, and that is the slight decrease in the torsion weight from the beginning to the end of most of the experiments, probably due to the slowing of the engine. By this means the torsion circle might lag behind. I made quite an investigation to see if this source of error existed, and came to the conclusion that it produced no perceptible effect. An examination of the different experiments shows this also; for in some of them the weight increases instead of decreases. See Tables XXXVII. to L.

The error from the formation of dew might also cause an apparent decrease; but I have convinced myself by experiment, and others can convince themselves from the tables, that this error is also inappreciable.

The observations seem to settle the point with regard to the specific heat at the  $4^{\circ}$  point within reasonable limits. There does not seem to be a change to any great extent at that point, but the specific heat decreases continuously through that point. It would hardly be possible to arrive at this so accurately as I have done by any method of mixture, for Pfaundler and Platter, who examined this point, could not obtain results within one per cent, while mine show the fact within a fraction of one per cent.

The point of minimum cannot be said to be known, though I have placed it provisionally between  $30^{\circ}$  and  $35^{\circ}$  C., but it may vary much from that.

The method of obtaining the specific heat of the calorimeter seems to be good. The use of solder introduces an uncertainty, but it is too small to affect the result appreciably. The different determinations of the specific heat of the calorimeter do not agree so well as they might; but the error in the equivalent resulting from this error is very small, and, besides, the mean result agrees well with the calculated result. It may be regarded as satisfactory.

The apparatus for determining the equivalent could scarcely be improved much, although perhaps the record of the torsion might be made automatic and continuous. The experiment, however, might be

improved in two ways; first, by the use of a motive power more regular in its action; and, second, by a more exact determination of the loss due to radiation. The effect of the irregularity of the engine has been calculated as about 1 in 4,000, and I suppose that the error due to it cannot be as much as that after applying the correction. The error due to radiation is nearly neutralized, at least between  $0^{\circ}$  and  $30^{\circ}$ , by using the jacket at different temperatures. There may be an error of a small amount at that point ( $30^{\circ}$ ) in the direction of making the mechanical equivalent too great, and the specific heat may keep on decreasing to even  $40^{\circ}$ .

Between the limits of  $15^{\circ}$  and  $25^{\circ}$  I feel almost certain that no subsequent experiments will change my values of the equivalent so much as two parts in one thousand, and even outside those limits, say between  $10^{\circ}$  and  $30^{\circ}$ , I doubt whether the figures will ever be changed much more than that amount.

It is my intention to continue the experiments, as well as work up the remainder of the old ones. I shall also use some liquids in the calorimeter other than water, and so have the equivalent in terms of more than one fluid.

BALTIMORE, 1878-79. Finished May 27, 1879.

## VL

## PROPOSITIONS IN COSMICAL PHYSICS.

BY BENJAMIN PEIRCE.

Presented October 8, 1879.

1. ALL stellar light emanates from super-heated gas. Hence the sun and stars are gaseous bodies.

2. Gaseous bodies, in the process of radiating light and heat, condense, and become hotter throughout their mass.

3. It is probable that their surfaces would become colder if there were not an external supply of heat from the collision of meteors.

4. Large celestial bodies are constantly deriving superficial heat from the collision of meteors, till at length the surface becomes super-heated gas, which constitution must finally extend through the mass.

5. Small celestial bodies are constantly cooling till they become invisible solid meteors.

6. The heat of space consists of two parts: first, that of radiation principally from the stars, which is small, except in the immediate vicinity of the stars; the second portion is derived from the velocity with which the meteors strike the planet at which the observation is taken; and this velocity partly depends upon the mass of the star by which the orbit of the planet is defined, and partly upon the mass of the planet itself.

7. If the planets were originally formed by the collision of meteors, it is difficult to account for an initial heat sufficient to liquefy them, and at the same time to account for their subsequent cooling, without a great change in the number and nature of the meteors; and any such hypothesis seems to invalidate the meteoric theory.

8. If the planets were not originally formed by the collision of meteors, their common direction of rotation becomes difficult of explanation.

## VII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.RESEARCHES ON THE SUBSTITUTED BENZYL COM-  
POUNDS.

## SIXTH PAPER.

THE ACTION OF BROMINE ON TOLUOL AND SOME OF ITS  
DERIVATIVES.

BY C. LORING JACKSON AND A. W. FIELD.

Presented June 12, 1878.

THE history of the action of halogens on toluol begins with the discovery of toluol by Pelletier and Walter, who say in their paper,\* published in 1838, on "retinnaphte" (toluol) from coal tar, that by distilling it repeatedly in a stream of chlorine there was formed a brownish-yellow oil with a sharp taste, a very strong smell somewhat like that of horse-radish, and a powerful action on the eyes, whose formula, founded on a doubtful analysis, was  $C_7H_6Cl_2$ , and which with potassic hydrate gave potassic chloride and an oil with a different smell. They also tried the action of bromine on boiling retinnaphte, and made in this way a compound similar to the preceding in every respect, but they observed that the cold hydrocarbon was apparently unaffected by chlorine.

Deville † was the next to take up the subject in 1841, in his paper on balsam of tolu, from which he obtained a hydrocarbon (benzoene) identical with the retinnaphte of Pelletier and Walter. From this he made the following compounds:  $C_7H_7Cl$ , boiling-point  $170^\circ$ , by the action of chlorine on the hydrocarbon when cooled and protected from light;  $C_7H_6Cl_4$  in diffused daylight;  $C_7H_5Cl_7$  when the chlorine was in excess;  $C_7H_6Cl_6$  in direct sunlight; and  $C_7H_5Cl_6$  by repeated distillation in an atmosphere of chlorine.

\* Ann. Chim. Phys., lxvii. 269.

† Ibid., ser. 3, iii. 178.

The next important step was taken by Cannizzaro,\* in 1855, who proved that the product of the action of chlorine on toluol is identical with benzylchloride made from benzylalcohol. Beilstein,† in 1860, introduced a great deal of confusion into the subject by contradicting Gerhardt's‡ inference from Deville's work, that the action of chlorine on cold toluol was different from its action on hot, and describing experiments of his own to prove that differences in temperature made no difference in the products. He also thought he had proved the identity of the dichlortoluol from toluol and chlorine with the chlorobenzol made from benzaldehyde with phosphoric pentachloride, but Cahours,§ three years later (1863), announced that they were only isomeric. In the same year (1863), Naquet|| studied trichlortoluol in comparison with the product of the action of phosphoric pentachloride on benzoylchloride.

The next important discovery was made in 1865 by Fittig and Glinzer,¶ who obtained monobromtoluol by treating cold toluol with bromine, and pointed out the marked differences between it and chlortoluol (benzylchloride); while in 1866 Kekule,\*\* in his paper on aromatic isomeres described benzylbromide made from benzylalcohol, and, after comparing it with monobromtoluol, explained the cause of their difference.

In this same year (1866), Beilstein, in conjunction with Geitner,†† put the whole subject on a firm basis by the following statement, since known as *Beilstein's Law*:—*Toluol behaves differently with chlorine according as it is hot or cold; in the cold, a chlortoluol as stable as chlorobenzol is formed, usually, however, mixed with benzylchloride unless great care is taken in cooling. If hot, the toluol is converted into benzylchloride, but it is not necessary absolutely to boil it, as a very slight increase of temperature is enough completely to prevent the formation of chlortoluol. With iodine only chlortoluol is formed under all conditions, even when the toluol is boiling; ‡‡ the chlortoluol obtained by this process is however contaminated with substances containing iodine. In this paper they predict a similar action with*

\* Ann. Chem. Pharm., xvi. 240.

‡ Traité de Chimie, iii. 567.

† Ibid., cxvi. 336.

§ Comptes Rendus, lvi. 222.

|| Comptes Rendus, lv. 407, lvi. 129.

¶ Ann. Chem. Pharm., cxxxiii. 47, cxxxvi. 301.

\*\* Ibid., cxxxvii. 188.

†† Ibid., cxxxix. 281.

‡‡ The use of iodine was suggested by the paper of H. Müller (Journal London Chem. Soc., xv. 41) on making chlorine substitution products from benzol in presence of iodine.

bromine, and state that xylol behaves with chlorine like toluol. A paper by Limpricht\* in the same volume of the *Annalen der Chemie und Pharmacie*, and another by Cannizzaro† in the next volume but one, did not advance the subject materially.

Lauth and Grimaux‡ in 1867, described a convenient form of the process for making benzylchloride, consisting in passing chlorine into toluol heated to 110°–140° in a flask with a return-cooler. In the same year, Beilstein§ extended his law to the action of bromine on toluol, which, if iodine was present, gave bromtoluol as the only product with the exception of a little of some iodine compound, even if the toluol was boiling, while without iodine bromine formed with boiling toluol benzylbromide, always, however, mixed with some bromtoluol. Lauth and Grimaux,|| on the other hand, could find no bromtoluol in the product obtained by mixing the vapors of bromine and toluol.

Since that time, but little progress has been made in this subject, the papers in which the action of halogens on toluol is mentioned, dealing rather with the products than with the conditions of the action, but the following papers deserve mention: Fittig,¶ on the formation of bromtoluol free from benzylbromide; Beilstein and Kuhlberg,\*\* extending Beilstein's Law to the action of chlorine on the various chlorine compounds of toluol, and one of their later papers†† (on tetrachlortoluol) in which they direct that 2 or 3 grs. of iodine should be used to make the chlorine enter the ring. This is the only statement of the amount of iodine needed for this purpose that we have been able to find, and even here nothing is said of the amount of toluol to be used with the 3 grs. of iodine.

We have not been more successful in finding definite statements about the temperature at which the bromine begins to enter the side-chain, those authors‡‡ who mention any temperature, give the boiling-point of the substance to be acted on, or a temperature somewhat above this, with the exception of Wachendorff,§§ who in studying the action of bromine on para- and metanitrotoluol, found that the benzyl-

\* Ann. Chem. Pharm., cxxxix. 808.    || Bull. Chem. Soc., vii. 108.

† Ibid., cxli. 198.

¶ Ann. Chem. Pharm., cxlvii. 39.

‡ Ibid., cxliii. 79.

\*\* Ibid., cxlvi. 317; also cxlvii. 339.

§ Ibid., cxliii. 869.

†† Ibid., cl. 286.

‡‡ Vogt and Henninger, Ann. Chim. Phys., ser. 4, xxvii. 130. Grimaux, Comptes Rendus, lxx. 1863. Radziszowski, Ber. d. ch. G., 1873, p. 492.

§§ Ann. Chem. Pharm., clxxxv. 259.



bromide was formed as low as  $130^{\circ}$  in a sealed tube, or at  $180^{\circ}$  in open vessels, while at its boiling-point the nitrotoluol was almost entirely decomposed by bromine.

In the work described in this paper, we have tried to give a more definite statement to Beilstein's Law, — which may be stated thus: When toluol (or its derivatives) is treated with chlorine or bromine in the cold, the halogen attaches itself to the benzole ring; if hot, to the side-chain; in presence of iodine exclusively to the ring, even when boiling. To do this, we have tried to determine the amount of benzylbromide formed from toluol and some of its derivatives, in the first place at different temperatures, and secondly in presence of different amounts of iodine.

#### *Effect of Differences in Temperature.*

In these experiments a weighed amount of toluol or the substituted toluol was heated in a flask with a return-cooler by a paraffine bath, and the calculated quantity of bromine added with a drop-funnel at such a rate that no bromine could be seen in the fumes which escaped through the cooler. The temperature of the bath and of the vapor within the flask was noted throughout the experiment. To determine how much benzylbromide had been formed, we used the following method, which is very similar to that used by Cannizzaro\* for the same purpose. The product of the reaction, after being freed from hydrobromic acid by washing first with a dilute solution of sodic carbonate and afterwards with distilled water, was heated to  $100^{\circ}$  with alcoholic ammonia for two hours; the bromides of ammonium and the three benzylamines thus formed were decomposed by warming with a solution of baric hydrate, and the amount of baric bromide determined by Volhardt's† sulphocyanate method of titration after the organic matter had been filtered out. To test the method of estimating the amount of removable bromine, pure parabrombenzylbromide was treated with alcoholic ammonia and baric hydrate, as described above, and 98 per cent of the calculated amount of bromine obtained. The experiments collected in Table I. were then made.

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\* Ann. Chem. Pharm., cxli. 198.

† Ibid., cxc. 1.

TABLE I.  
ACTION OF BROMINE ON TOLUOL. BOILING-POINT, 111°.

Number of Experiment.	Amount taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
I.	5 grs.	100°	97°-98°	72.	65
II.	5 grs.	100°	98°-100°	54.	20
III.	10 grs.	100°	97°-98°	55.	60
IV.	10 grs.	100°	95°	65.	55
V.	5 grs.	120°	110°-114°	82.	10
VI.	10 grs.	120°	112°-114°	87.	20
VII.	10 grs.	120°	111°-118°	74.	20

ACTION OF BROMINE ON PARACHLORTOLUOL. MELTING-POINT, 7°; BOILING-POINT, 160°.

Number of Experiment.	Amount taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
VIII.	6.9 grs.	100°	81°-86°	69.	45
IX.	"	120°	110°-113°	80.	
X.	"	140°	130°-135°	92.	20
XI.	"	167°	157°-161°	95.	15

ACTION OF BROMINE ON PARABROMTOLUOL. MELTING-POINT, 28°.5; BOILING-POINT, 185°.

Number of Experiment.	Amount taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
XII.	9.4 grs.	100°	87°-92°	51.	
XIII.	"	100°	90°-98°	58.	40
XIV.	"	120°	111°-114°	95.	25
XV.	"	120°	110°-114°	90.	30
XVI.	"	140°	130°-134°	88.	10
XVII.	"	170°	160°-164°	92.	8
XVIII.	"	190°	180°-184°	94.	5

ACTION OF BROMINE ON ORTHOBROMTOLUOL. BOILING-POINT, 182°.

Number of Experiment.	Amount taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
XIX.	9.4 grs.	100°	90°	21.	30
XX.	"	100°	86°-92°	31.	45
XXI.	"	100°	90°	32.	55
XXII.	"	120°	110°-114°	74.	50
XXIII.	"	140°	130°-134°	88.	25
XXIV.	"	170°	160°-164°	84.	10
XXV.	"	190°	180°-184°	84.	15

Before considering the inferences which can be drawn from these results, it is necessary to examine the sources of error which affect the accuracy of the process; and, for this purpose, all the results obtained under the same conditions are collected in Table II.

TABLE II.

TOLUOL AT 100°. 5 grs. used.			TOLUOL AT 120°. 10 grs. used.		
No. of Experiment.	Time in Minutes.	Per cent.	No. of Experiment.	Time in Minutes.	Per cent.
I.	65	72	VI.	20	87
II.	20	54	VII.	20	74
TOLUOL AT 100°. 10 grs. used.			PARABROMTOLUOL AT 120°.		
III.	60	55	XIV.	25	95
IV.	55	65	XV.	30	90.
TOLUOL AT 120°. 5 grs. used.			ORTHOBROMTOLUOL AT 100°.		
V.	10	82	XIX.	30	21
			XX.	45	31
			XXI.	55	32

The want of agreement between these results can be ascribed to two causes: first, differences in the rate of adding the bromine; second, unavoidable defects in the method of bromining or of treating the product. To the first class belong the difference of 18 per cent, corresponding to 45 minutes difference in rate between Nos. I. and II., and that of 10 per cent, corresponding to 15 minutes between Nos. XIX. and XX.; but these are the only differences that come under this class, a difference of less than 10 minutes having apparently no effect upon the amount of benzylbromide formed (see XX. and XXI.). The differences due to the second cause are that of 10 per cent between III. and IV., 13 per cent between VI. and VII., and 5 per cent between XIV. and XV., which show that our method is incapable of giving the exact quantitative results that we had hoped for. The most probable cause of these variations is the difficulty of washing and handling the liquid or pasty product of the bromining. In the following discussion, Experiment I. will be rejected, because of the very slow rate at which the bromine was added, and differences of less than 10 per cent will be accepted, if at all, only with the greatest caution.

*Effect of the Temperature on the Amount of Benzylbromide formed.*  
—To make this comparison easier, the results given in Table I. (reduced to the mean where there are several observations at the same temperature) are collected in the following table, and in the second

column, under each substance, the differences between the percentages at each temperature, and at that which immediately follows it, are given.

TABLE III

Temperature.	Toluol.		Parachlortoluol.		Parabromtoluol.		Orthobromtoluol.	
	Per cent.	Difference.	Per cent.	Difference.	Per cent.	Difference.	Per cent.	Difference.
81°-100°	58	23	69	11	54	88	28	46
110°-114°	81		80	-12	92	-4	74	9
130°-135°			92	8	88	4	83	1
160°-164°			96		92	2	84	0
180°-184°				15	94	2	84	10
110°-Bpt.								

From this it appears that the bromine begins to enter the side-chain in considerable quantity at about the boiling-point of toluol (111°), and that after this the amount of benzylbromide formed increases with the temperature, although to a much smaller extent, with the exception of parabromtoluol, which is probably due to defects in the process; in fact, the difference between 81°-100° and 110°-114° is greater than that between the latter temperature and the boiling-point of the substance, except in the case of the single series of observations on parachlortoluol.

Some experiments with paraiodtoluol cannot be directly compared with the preceding, because we could find no satisfactory way of removing the iodine set free during the addition of the bromine, and were therefore obliged to content ourselves with weighing the crystals of paraiodbenzylbromide formed. We found, under these conditions, that below 100° no crystals were formed; at about 111°, 18 per cent of the calculated amount was obtained; at 135°, 42 per cent; at 175°, 54 per cent; at 200°, 51 per cent. The low percentages are partly accounted for by the solubility of the paraiodbenzylbromide in the oily secondary products. A similar series with parachlortoluol gave below 100° no crystals; at 111°, 89 per cent of very impure crystals (apparently nearly one half parachlortoluol); at 135°, 98 per cent of purer crystals; at 160°, 89 per cent. These results confirm, in a general way, those obtained by the more accurate method.

*The effect of differences in temperature on the rate at which the bromine is taken up will be seen from the following table, in which the*

mean time needed to bromir equivalent weights of the substances for each temperature is given. In calculating these means, the times of several experiments were used, in which the amount of benzylbromide was not determined; many of them, therefore, depend on a much larger number of observations than the mean amounts given in Table III.

TABLE IV.

Temperature.	TIME IN MINUTES.			
	Toluol.	Parachlortoluol.	Parabromtoluol.	Orthobromtoluol.
81°-100°	26	40	43	43
110°-114°	11	30	27	40
130°-135°		22	10	26
160°-164°		20	8	10
180°-184°			5	15

Although the method of adding the bromine used by us made great differences of rate, under the same conditions, possible, so that all these results must be taken with some caution, it is evident that the rate increases rapidly, and apparently regularly, with the temperature, showing no especially large increase between 81°-100° and 110°-114°, as was the case with the per cent. This rapid increase in the rate suggests the following objection to the results obtained in studying the effect of temperature on the amount of benzylbromide formed; the small percentages of benzylbromide obtained below 100° may have been due to loss of bromine from running the experiment too fast, as the secondary products were not studied; and therefore it is possible that they were the unaltered original substance, and not formed from this by substitution of bromine in the ring; this view is supported by the larger per cent (72) obtained in Experiment I., where the time was 45 minutes longer than in II.; but, on the other hand, it is hardly possible that nearly 5 grs. of bromine could have escaped without giving a perceptible color to about the same quantity of hydrobromic acid, and great pains were taken in every experiment to regulate the addition of the bromine so that the escaping fumes should be perfectly colorless. Even if the amounts of benzylbromide obtained below 100° are rejected on this account, our statement that there is a decided change in the action at 111° still holds good, as in that case the time necessary to take up the bromine below 100° must be greatly increased, and therefore the differences in rate between 87°-100° and 110°-114° would become as great in proportion to the differences between

other temperatures as those in the per cents are if our present results are accepted.

We had hoped, in beginning this research, to make a careful comparison of the action of bromine on toluol and its substitution products, but the differences between the results from different substances fall so near the wide limits of error of our process, that we prefer to confine ourselves to the following very general statements. Bromine is taken up by toluol more rapidly than by any of its substitution products studied; orthobromtoluol seems to take up bromine less rapidly than parabromtoluol, and this inference from our quantitative results is confirmed by our experience in the preparation of the substituted benzylbromides in large quantity, when it has been observed invariably that the parabromtoluol absorbed bromine most rapidly, the meta-compound less so, and the orthobromtoluol even more slowly than the meta. In regard to the percentages of benzylbromide formed from each substance we do not feel that our results allow us to make any generalization, as the apparently lower numbers obtained from the orthobromtoluol may be due to differences in working up the product, which in the case of the ortho-compound is a liquid, while the parabromtoluol yields a pasty solid.

We have also tried some experiments with toluol at lower temperatures, and found that at  $58^{\circ}$ , and even at  $0^{\circ}$ , a small amount of benzylbromide was formed, as shown by obtaining an amine on treatment of the product with alcoholic ammonia. The rate at which the bromine was taken up was, however, extremely slow, and we feel that these experiments need confirmation.

#### *Effect of the Addition of Iodine.*

We were induced to take up this branch of the subject by the observation that paraiodbenzylbromide was formed by the action of bromine on paraiodtoluol, even when the flask was filled with violet vapors of iodine during the addition of the bromine, which contradicted Beilstein's Law as generally understood; but we have not studied it so thoroughly as the effect of differences in temperature, as we could find no sufficiently satisfactory and easy method of determining the amount of benzylbromide formed.

Our best series of results (Table V.) was obtained from parachlortoluol bromided at  $160^{\circ}$ , the crystals of parachlorbenzylbromide formed being weighed after they had been brought to the melting-point of the pure substance,  $48^{\circ}.5$ .

TABLE V.

Per cent of Iodine added.	10 grs. Parachlorotoluol yielded.	Per cent of possible Amount.
1	6.5 grs.	51
5	3. grs.	23
10	No crystals.	

The product of the last experiment was washed, boiled with alcoholic sodic acetate, and then heated in a sealed tube with aqueous ammonia, when crystals of the parachlorbenzylalcohol were obtained, showing that even in presence of 10 per cent of iodine a portion of the bromine enters the side-chain. This result was confirmed by some experiments on toluol, in one of which toluol was mixed with 10 per cent of iodine and treated with chlorine at  $120^{\circ}$ ; on fractioning the product, about one half passed over from  $164^{\circ}$ – $222^{\circ}$  (chlorotoluol boils from  $156^{\circ}$ – $160^{\circ}$ ), attacked the nose violently, and gave an amine when heated in a sealed tube with alcoholic ammonia; it must, therefore, have contained benzylchloride, boiling-point  $176^{\circ}$ , and probably chlorbenzylchloride, boiling-point  $213^{\circ}$ . In another experiment it seemed that even 40 per cent of iodine was not enough to completely prevent the formation of benzylbromide at  $111^{\circ}$ ; but the determination of the benzylbromide by the amine process was interfered with by the presence of iodine substitution products to such an extent that we can place but little reliance on this result.

#### *Summary.*

I. The portion of Beilstein's Law which states that benzyl-compounds are formed at high, and substituted toluols at low temperatures, is confirmed by our experiments.

II. The benzyl-compound begins to be the principal product near the boiling-point of toluol ( $111^{\circ}$ ); in other words, no connection can be traced between the boiling-point of a substituted toluol and the temperature at which the bromine begins to enter its side-chain in quantity. Above  $111^{\circ}$  there is a gradual increase in the amount formed as the temperature is raised; but the total increase from  $111^{\circ}$  to the boiling-point of the substance is usually smaller than the increase from  $100^{\circ}$  to  $111^{\circ}$ .

III. The rate at which the bromine is taken up becomes more rapid as the temperature is raised.

IV. Toluol takes up bromine more rapidly than its substitution pro-

ducts. This result is confirmed by the observation of Beilstein and Kuhlberg,\* that the more chlorine there was attached to the ring, the harder it was to introduce chlorine into the side-chain.

V. The monobromtoluols seem to take up bromine (in the side-chain) in the following order: para most rapidly, meta next, ortho least rapidly.

VI. The portion of Beilstein's Law which states that in presence of iodine no benzyl-compound is formed, even at the boiling-point, is not true when the amount of iodine is 10 per cent or less, and it is probable that toluol yields a little benzylbromide at 111°, even in presence of 40 per cent of iodine.

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From our experiments, it follows that the best way of obtaining a benzylbromide is to add the bromine at the boiling-point of the substance used, but it is not well to allow the temperature to rise above this point, as then there is danger of decomposition of the product.

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\* Ann. Chem. Pharm., cl. 286.



## VIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.RESEARCHES ON THE SUBSTITUTED BENZYL COM-  
POUNDS.

## SEVENTH PAPER.

## ORTHOBROMBENZYL COMPOUNDS.

BY C. LORING JACKSON AND J. FLEMING WHITE.

Presented November 12, 1879.

THE substances described in this paper are the first substituted benzyl compounds belonging to the ortho series known; unless, indeed, the orthochlorbenzaldehyde, made from salicylic aldehyde,\* be included in this class. They were made from the orthobrombenzylbromide,† which was described in the first paper of this series as an oily liquid that did not solidify even at  $-15^{\circ}$ . The specimen on which that experiment was tried could not have been perfectly pure, as we have since found that the orthobrombenzylbromide solidifies near zero in large rhombic crystals, often one centimeter in diameter, which melt at  $30\frac{1}{4}^{\circ}$ , and can be recrystallized from alcohol or ligroine. An analysis gave the following result:—

0.3570 gr. of substance gave 0.5380 gr. AgBr.

	Calculated for $C_6H_4BrCH_2OH$ .	Found.
Bromine	64.00	64.13

*Orthobrombenzylalcohol*,  $C_6H_4BrCH_2OH$ , was made by the action of aqueous ammonia at  $160^{\circ}$  in a sealed tube on the acetate obtained by boiling the bromide with an alcoholic solution of sodic acetate. As its melting-point ( $80^{\circ}$ ) was much higher than expected, we also prepared

\* Henry, Ber. d. ch. G., 1869, p. 136.

† These Proceedings, Vol. XII p. 217.

it by heating the acetate with alcoholic potassic hydrate in a sealed tube, and by boiling the bromide with water for two days; and found that the products of all these methods melted at the same point ( $80^{\circ}$ ), so there can be no doubt that this is the true melting-point of the alcohol. An analysis of the substance made by the first method gave the following results:—

0.5543 gr. of substance dried *in vacuo* gave on combustion 0.9131 gr.  $\text{CO}_2$  and 0.1990 gr.  $\text{H}_2\text{O}$ .

0.3480 gr. gave, by the method of Carius, 0.3498 AgBr.

	Calculated for $\text{C}_7\text{H}_6\text{BrOH}$ .	Found.
Carbon	44.92	44.94
Hydrogen	3.74	3.99
Bromine	42.79	42.78

*Properties.* Slightly flattened white needles, sometimes 5 cm. long, when crystallized from boiling water, from ligroine needles grouped in sheaves, with but little odor, which melt at  $80^{\circ}$ , sublime in oily drops, and distil with steam very easily. It is very slightly soluble in cold, much more so in hot water or ligroine, and freely in alcohol, ether, benzol, glacial acetic acid, and carbonic disulphide. It can be most conveniently purified by crystallization from hot ligroine. Oxidized with potassic permanganate, it gave orthobrombenzoic acid, melting point  $147^{\circ}$ – $148^{\circ}$ .

The *Orthobrombenzylcyanide*, prepared by boiling alcoholic potassic cyanide with the bromide, was a dark-colored oil, which did not solidify in a freezing mixture, and seemed to be decomposed by distillation; we therefore did not attempt to purify and analyze it.

The *Orthobromalpatoluylic Acid*,  $\text{C}_6\text{H}_4\text{BrCH}_2\text{COOH}$ , was made from the cyanide by heating it with strong hydrochloric acid to  $130^{\circ}$  in a sealed tube. The product was purified by conversion into the ammonium salt, and recrystallization from water or alcohol of the acid set free from this by dilute sulphuric acid.

It forms white pearly plates, or flattened needles, melting at  $102\frac{1}{2}^{\circ}$ – $103^{\circ}$ ; but little soluble in cold, more so in hot water, freely in alcohol, ether, benzol, glacial acetic acid, and carbonic disulphide. It is only sparingly soluble in cold ligroine, but very soluble in hot, from which it crystallizes in small needles arranged in fan-shaped groups.

*Argentie Orthobromalpatoluylate*,  $\text{C}_6\text{H}_4\text{BrCH}_2\text{COOAg}$ , made from the acid by adding ammonic hydrate, driving off the excess of ammonia on the water-bath, and precipitating with argentic nitrate, formed a

white mass made up of small needles. It was washed with water, dried *in vacuo*, and analyzed.

0.2686 gr. of the salt gave 0.1200 gr. AgCl.

	Calculated for $C_8H_5BrO_2Ag$ .	Found.
Silver	33.54	33.62

It is slightly soluble in boiling water, freely in dilute nitric acid.

*Calcic Orthobromalphatoluylate*,  $Ca(C_6H_4BrCH_2COO)_2$ , made by boiling an aqueous solution of the acid with calcic carbonate, and evaporating the filtrate, gave, dried *in vacuo*, the following result:—

0.24969 gr. of the salt gave 0.0300 gr. CaO.

	Calculated for $(C_6H_4BrO_2)_2Ca$ .	Found.
Calcium	8.54	8.58

It crystallizes from a very concentrated hot solution in circular groups of radiating needles, very soluble in water, somewhat less so in alcohol.

The *barium* salt formed an amorphous mass, like varnish.

A solution of the ammonium salt gave the following precipitates: with a salt of copper, *bluish green*; with ferric chloride, *orange brown*; with mercurous or plumbic salts, *white*; all of which resembled those obtained with the parabromalphatoluylic acid.

*Orthobrombenzylsulphocyanate*,  $C_6H_4BrCH_2SCN$ , is an oil which does not solidify in a freezing mixture of snow and salt. It was not analyzed.

*Orthobrombenzylamines*. The product of the action of alcoholic ammonia on orthobrombenzylbromide at  $100^\circ$ , for two hours, consisted of crystals of the tertiary amine, and a liquid containing the primary and secondary amines and ammonia, with their bromides. After filtering, the crystals were washed with cold alcohol, sodic hydrate, and finally water, and then recrystallized from warm ether till they gave a constant melting-point ( $121\frac{1}{2}^\circ - 122^\circ$ ). The filtrate from the crystals was evaporated to dryness, and treated with carbonic dioxide to convert any free primary amine into carbonate. Upon washing with water, the salts of the primary amine and ammonia dissolved, leaving the secondary amine as an oil, which, after washing with sodic hydrate, was converted into the chlorplatinate by addition of chlorplatinic acid to its alcoholic solution. To the filtrate from the secondary amine, sodic hydrate was added, and the oily primary amine thus obtained washed with water until it was free from ammonia, care being taken not to expose it to the carbonic dioxide of the air.

*Monorthobrombenzylamine*,  $C_6H_4BrCH_2NH_2$ , is a colorless oil, insoluble in water, but soluble in ether, which absorbs carbonic dioxide from the air very readily, becoming converted into the carbonate.

The *carbonate*, made most easily by allowing an ethereal solution of the free base to evaporate in the air, forms small white crystals; melting-point,  $95^\circ$ ; and is soluble in water and alcohol.

The *chloride*, made by adding hydrochloric acid to the carbonate, crystallizes in white radiating needles, or from alcohol in small curled needles; melting-point,  $208^\circ$ ; and is soluble in water and alcohol.

The *chlorplatinate*,  $(C_6H_4BrCH_2NH_2)_2PtCl_6$ , is precipitated on adding chlorplatonic acid to the free base; an analysis gave

0.1990 gr. of substance gave 0.0505 gr. Pt.

	Calculated for $[C_6H_4BrCH_2NH_2)_2PtCl_6$ .	Found.
Platinum	25.16	25.38

It forms indistinct orange-yellow needles, sparingly soluble in water, decidedly so in alcohol, and insoluble in ether.

The *Diorthobrombenzylamine* was made by treating the chlorplatinate with sulphuretted hydrogen, washing the chloride out of the platonic sulphide with hot alcohol, and precipitating the free base with sodic hydrate from the solid chloride. In this way an oil was obtained, which solidified after some time in well-marked rhombic crystals, with an agreeable smell, melting at  $36^\circ$ , and soluble in all the ordinary solvents, with the exception of water.

*Diorthobrombenzylamine Chlorplatinate*,  $[(C_6H_4BrCH_2)_2NH_2)_2PtCl_6$ , prepared as already described, was purified by washing with alcohol and water, dried at  $70^\circ$ , and analyzed.

0.5840 gr. of the salt gave 0.1030 gr. Pt.

	Calculated for $[(C_6H_4Br)_2NH_2)_2PtCl_6$ .	Found.
Platinum	17.58	17.66

A yellow obscurely crystalline precipitate, slightly soluble in water and alcohol, insoluble in ether.

The *chloride* made by adding hydrochloric acid to an alcoholic solution of the free base separates out as the alcohol evaporates in groups made up of a few radiating white needles, which melt at  $166^\circ$ , are but slightly soluble in cold water, more soluble in hot and in alcohol, sparingly in ether.

*Tetrorthobrombenzylamine*,  $(C_6H_4BrCH_2)_4N$ , gave the following result on analysis:—

0.3245 gr. of substance gave 0.3488 gr. AgBr.

	Calculated for $(C_7H_6Br)_3N$ .	Found.
Bromine	45.80	45.73

It forms small prisms with an adamantine lustre, melting at  $121\frac{1}{2}^{\circ}$ – $122^{\circ}$  and subliming in oily drops; almost insoluble in  $H_2O$  and alcohol; slightly soluble in cold, freely in hot ligroine, and in ether and benzol.

*Triorthobromobenzylamine Chlorplatinat*e,  $[(C_6H_4BrCH_2)_3NH]_2PtCl_6$ , made by adding chlorplatinic acid to an ethereal solution of the amine, gave the following result on analysis:—

0.39708 gr. of the salt gave 0.0540 gr. Pt.

	Calculated for $[(C_6H_4Br)_3NH]_2PtCl_6$ .	Found.
Platinum	13.51	13.60

A whitish yellow, barely crystalline precipitate, insoluble in water and ether, and very slightly, if at all, soluble in alcohol.

On boiling the tertiary amine with dilute alcohol and hydrochloric acid, it dissolved, and on cooling deposited white spheres made up of radiated needles; but an analysis of the substance gave an amount of chlorine too low for the pure chloride, and we did not think the compound of sufficient importance to study it further.

## IX.

BRIEF CONTRIBUTIONS FROM THE PHYSICAL LABORATORY  
OF HARVARD COLLEGE, UNDER THE DIRECTION OF PRO-  
FESSOR JOHN TROWBRIDGE.

No. XVI.—A NEW METHOD OF STUDYING WAVE  
MOTIONS.

By H. H. EUSTIS.

Presented May 14, 1879.

THE plan of Niemoller for interrupting in a regular manner an electric circuit affords also a convenient method of studying wave motion on the surface of mercury. The method of Niemoller consists in providing a stretched iron wire, through which a current flows, with a platinum point at its middle, which dips in mercury, and placing a magnet above and near the middle of the half of the wire through which the current flows. The wire, once set in vibration, is maintained in motion by the attraction of the magnet. I substituted a large shallow evaporating dish filled with clean mercury for the small connecting cup used by Niemoller, and an electro-magnet for his permanent magnet. Since the electro-magnet consisted of a number of coarse wire coils, and formed part of the circuit with the iron wire, a bright spark was produced at the break, on the surface of the mercury. The mercury was then covered with an extremely fine layer of lycopodium dust, which was effected by blowing off the lycopodium after it had been sifted over the mercury. When the wire was set in vibration, beautiful rings, very similar in appearance to Newton's rings, emanated from the point where the break was made, and spread out over the surface of the mercury. These rings were almost as sharply defined as Newton's rings, and were due to the illumination of the waves by the reflection of the light of the electric spark from the fine particles of lycopodium dust. The regularity of the rings of light made it possible to measure their radii, and in this way determine the rate of vibration of different lengths of wires. The follow-

ing numbers represent one of several measurements which I made on wire of the same diameter:—

Wire 100 cm. in length . . . . .	2 waves to 5 mm.
“ 50 cm. “ . . . . .	4 “ “

Thus the wave lengths were found to be proportional to the lengths of the wire. The interference of waves in an elliptical vessel, caused by producing the vibrations at the two foci, and described by the brothers Weber in their *Wellenlehre*, can be beautifully shown by this method.

## NO. XVII.—VIBRATIONS OF CIRCULAR AND ELLIPTICAL PLATES.

BY FRANCIS E. CABOT.

Presented May 14, 1879.

THE experiments from which the results given in the following paper were obtained were made with the idea of finding out whether a change in the ellipticity of a plate would have any effect on the nodal lines of such a plate.

I had seven plates of the same material, of equal thickness: one was a circle with a diameter of eight inches, and the others were ellipses, all having their major axes eight inches in length, and their minor axes decreasing, each by an inch, from seven to two inches in length. The ellipses I clamped close to the edge at both extremities of the minor axis. They were bowed at one extremity of the major axis. The circle was clamped close to the edge, at both extremities of a diameter, and bowed at 90° from the clamp.

Under these conditions, the nodal lines gave a series of similarly situated curves, which changed their curvature and position correspondingly to the change in the ellipticity of the plates. The circle gave a star-shaped figure with six points connected by curves of nearly equal curvature (Fig. 1). The ellipse whose minor axis was seven inches in length gave a line nearly an inch in breadth from the clamp to the point of clamping with two whose ends were equally distant from the major axis at the edge of the plate (Fig. 2). The curves, as we see by the figures, are of nearly the same curvature as the curves

connecting the points of the star given by the circle. But in the next plate (Fig. 3), whose minor axis is six inches in length, the curves, though situated similarly to those in the last figure, are of a much smaller curvature. This decrease continues as the minor axis decreases, until, as we see in Fig. 5, the lines have become nearly, if not quite, straight.

Another point to be noticed is that in Fig. 4 we begin to see that

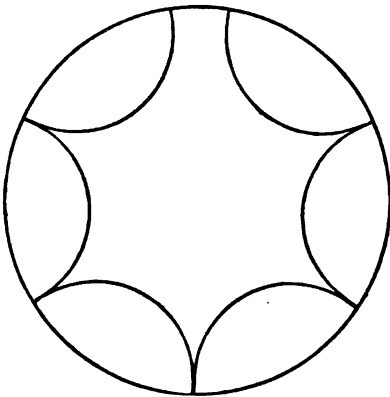


Fig. 1.

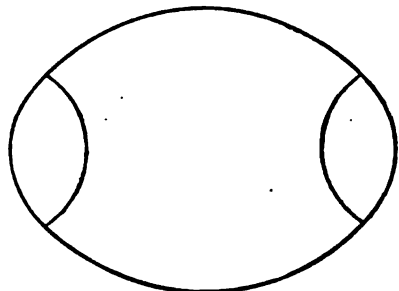


Fig. 3.

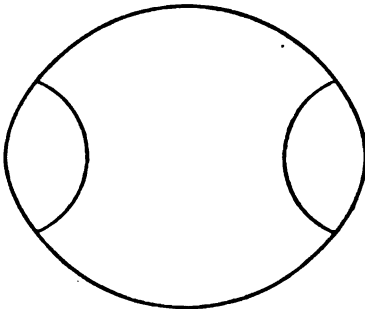


Fig. 2.

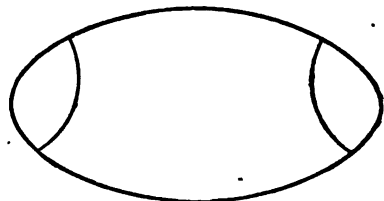


Fig. 4.



Fig. 5.

the extremities of the curves are nearer together on the side where the clamp is than on the side damped by the finger, and this fact becomes very noticeable in Fig. 5.

I also made a series of experiments with the same plates, clamped at one edge, damped in the centre, and bowed at a point about  $70^\circ$  from that extremity of the minor axis which was not clamped. Here, too, I obtained a series of curves similar to each other (Figs. 6 to 9),



but differing largely from the last series, though we may notice that Fig. 9 resembles Fig. 5.

These two series of curves show conclusively that the arrangement of the curves is not materially altered by a change in the ellipticity when the plate is bowed at the edge, but that the curvature of the curves does correspond very closely to the change in the ellipticity of the plate. Furthermore, that the nearer the plate comes to a straight bar, the more the figures in the two series resemble each other; show-

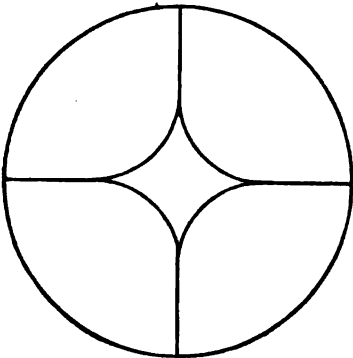


Fig. 6.

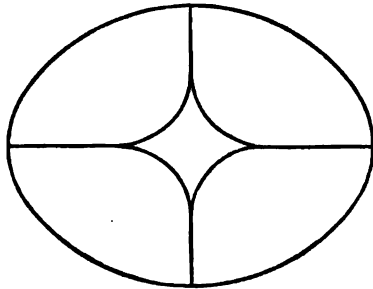


Fig. 7.

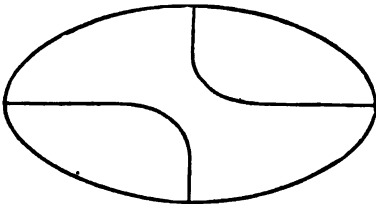


Fig. 8.

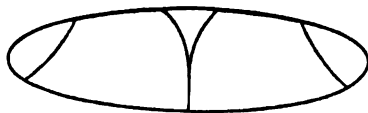


Fig. 9.

ing that the nearer the plate is to a circle, the more various are the figures obtained by damping and bowing in different places.

I also tried to obtain a series of similar curves by exciting the vibrations through a hole bored in the centre of the plate. But in this I failed; I could get a set of curves for two or three consecutive plates, but not throughout the whole set of plates. One fact which was particularly noticeable in connection with this set of experiments was, that five or six sets of curves resulted from bowing the same plate in apparently exactly the same way, although the plate gave a different note for each set of curves.

The results of these experiments can be summed up as follows :—

1. Certain fundamental vibrations of elliptical plates are not changed by wide variations in the ellipticity of the plates.
  2. The vibrations of elliptical plates are less varied than those of circular plates. A small amount of ellipticity results in a quick and marked limitation in the variety of the vibrations of the plate.
  3. It is to be conjectured, therefore, that an animal, whose ear is provided with an elliptical-shaped membrane, if such an animal exists, has less perfect powers of hearing than one provided with a circular membrane, as far as the variety of vibration of the membranes are considered.
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## NO. XVIII — PERFORATED VIBRATING DISCS.

BY FRANCIS E. CABOT.

Presented Dec. 10, 1879.

SINCE the membrane of the human ear is often perforated in auricular surgery without the destruction of the sense of hearing, at the suggestion of Professor Trowbridge I tried the effect of the removal of a large portion of the vibrating disc of a telephone. Three discs were made of ordinary tin-type plate; one with a hole in the centre half an inch in diameter; one with four holes, each half an inch in diameter, with their centres on two lines at right angles, crossing in the centre of the plate, and half-way from the centre to the edge of the disc; the third with four holes four fifths of an inch in diameter, and placed similarly to those last mentioned. Substituting these discs for the discs ordinarily used in a Bell telephone, I found that messages could be sent and received, but in a somewhat imperfect manner. On covering the holes with paper, I found that I could use either of the last two plates, in either the sending or receiving telephone, or in both, with nearly, if not quite, as good results as with the unperforated discs commonly used.

The disc with the hole in the centre did not give good results, as was to be expected, since the iron was taken away just in front of the magnet; but the others worked very well indeed. I also found that a disc of mica of the same size as the usual plate, with a piece of the

ordinary plate, the size of a cent, fastened to its centre, could be used either as a receiving or sending disc over a short line; but it did not articulate very well; this defect, however, may have been caused by the want of homogeneity in the mica. The results of my experiments show that we can remove nearly one third of the iron plate (the whole plate being two inches and a half in diameter) without seriously injuring the articulation; and, furthermore, that a piece of iron three quarters of an inch in diameter is sufficient to cause a plate of mica two inches and a half in diameter to articulate partially and sufficiently to be heard over a short line.

# No. XIX. — ON A STANDARD FOR ESTIMATING THE AMOUNT OF LIGHT REFLECTED BY VARIOUS SUBSTANCES.

By A. H. LEE.

Presented Dec. 10, 1879.

THE following experiments were undertaken with the view of obtaining a standard reflecting surface, with which the light reflected from various reflecting surfaces could be compared. I have collected various experiments with white paper, tinted paper, and silvered surfaces.

At first I used the photometer due to Professor Pickering, and described in his work on *Physical Manipulations*, Vol. I. p. 132. L is a candle;  $\alpha$  and  $\beta$  are two mirrors, which reflect the light of the candle to the Bunsen disc A, which slides between the mirrors  $\alpha$  and  $\beta$ .

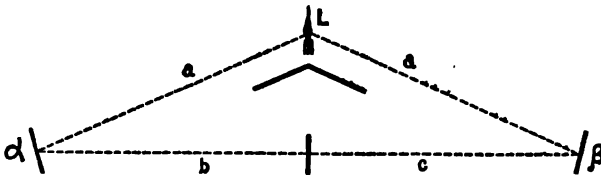


Fig. 1.

If  $I$  represents the reflection from mirror  $\alpha$ , and  $I'$  that from  $\beta$ , we have at A

$$\frac{I}{(a+b)^2} = \frac{I'}{(a+c)^2}; \text{ or } I = \frac{(a+b)^2}{(a+c)^2} I'.$$

*Percentage of Light reflected from Different Substances.*

Experiments with one candle comparing the reflective power of paper and a mirror. (Fig. 1.) Paper was foolscap.

Obs.	Dist. $a + b$ .	Dist. $c$ .	Ratios.
1	73	64	$\frac{5329}{14841} = 3.57$
2	76	61	$\frac{5776}{13904} = 4.15$
3	75	62	$\frac{5625}{14241} = 3.95$
4	75	62	" = 3.95
5	74	63	$\frac{5476}{14400} = 3.80$
6	77	60	$\frac{5929}{15809} = 3.75$
7	76	61	$\frac{5776}{13904} = 4.15$
8	76	61	" = 4.15
9	76	61	" = 4.15
10	76	61	" = 4.15

Percentage in terms of reflection of mirror . . . .40458

*Percentage of Total Light reflected from a Mirror.*

Experiments with two candles. (Fig. 2.) In the following experiments a candle was substituted for the mirror at  $\alpha$ , in order to get the percentage of total light reflected, eliminating the coefficient of

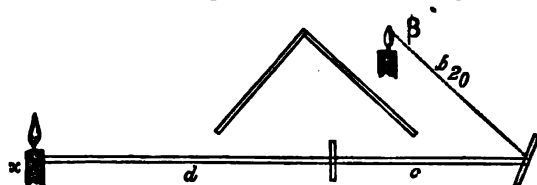


Fig. 2.

reflection of a mirror. To eliminate the error which might arise from unequal combustion, the candles were changed about during each observation, and the average of the two ratios taken. The following are the results:—

Candle.	Position.	Dist. $d$ .	Dist. $b + c$ .	Ratios.	Averages.
A	$\alpha$	56	44	$1.27$	$1.78$ (1)
B	$\alpha$	58	42	$1.35$	
A	$\alpha$	56	44	$1.27$	$1.32$ (2)
B	$\alpha$	59	41	$1.37$	

Candle.	Position.	Dist. <i>d</i> .	Dist. <i>b</i> + <i>c</i> .	Ratios.	Averages.
<i>A</i>	<i>a</i>	57	43	$\frac{1.78}{1.38}$	$\frac{1.78}{1.38}$ (3)
<i>B</i>	<i>a</i>	53	47	$\frac{1.38}{1.78}$	
<i>A</i>	<i>a</i>	58	42	$\frac{1.38}{1.78}$	$\frac{1.78}{1.38}$ (4)
<i>B</i>	<i>a</i>	56	44	$\frac{1.78}{1.38}$	
<i>A</i>	<i>a</i>	56	44	$\frac{1.38}{1.78}$	$\frac{1.78}{1.38}$ (5)
<i>B</i>	<i>a</i>	55	45	$\frac{1.78}{1.38}$	
<i>A</i>	<i>a</i>	58	42	$\frac{1.38}{1.78}$	$\frac{1.78}{1.38}$ (6)
<i>B</i>	<i>a</i>	57	43	$\frac{1.78}{1.38}$	
Percentage (average of six observations)					.586

FOOLSCAP.

Candle.	Position.	Dist. <i>d</i> .	Dist. <i>b</i> + <i>c</i> .	Ratios.	Averages.
<i>A</i>	<i>a</i>	67	33	$\frac{1}{2.1}$	$\frac{1}{2.1}$ (1)
<i>B</i>	<i>a</i>	67	33	$\frac{1}{2.1}$	
<i>A</i>	<i>a</i>	66	34	$\frac{1.78}{2.38}$	$\frac{1.38}{2.38}$ (2)
<i>B</i>	<i>a</i>	69	31	$\frac{1.38}{2.38}$	
<i>A</i>	<i>a</i>	68	32	$\frac{1.38}{2.1}$	$\frac{1.78}{2.38}$ (3)
<i>B</i>	<i>a</i>	66	34	$\frac{1.78}{2.38}$	
<i>A</i>	<i>a</i>	67	33	$\frac{1}{2.1}$	$\frac{1}{2.1}$ (4)
<i>B</i>	<i>a</i>	67	33	$\frac{1}{2.1}$	
<i>A</i>	<i>a</i>	67	33	$\frac{1}{2.1}$	$\frac{1.38}{2.38}$ (5)
<i>B</i>	<i>a</i>	68	32	$\frac{1.38}{2.1}$	
<i>A</i>	<i>a</i>	67	33	$\frac{1}{2.1}$	$\frac{1.78}{2.38}$ (6)
<i>B</i>	<i>a</i>	66	34	$\frac{1.78}{2.38}$	

Percentage (average of six observations)					.2309
" of light reflected from paper compared					
with mirror					.405
Percentage of total light reflected from mirror					.586
" of total light reflected from paper.					.2373
" " " " " by di-					
rect experiment					.2309

Difference . . . . .0064

The above result is rather a remarkable confirmation of the correctness of the theory of this method of measuring reflection.

*Percentage of Total Light reflected from Colored Papers.*

## GREEN.

Candle.	Position.	Dist. <i>d</i> .	Dist. <i>b</i> + <i>c</i> .	Ratios.	Averages.
<i>A</i>	<i>a</i>	70	30	$\frac{5.444}{5.444}$	$\frac{5.444}{5.444}$ (1)
<i>B</i>	<i>a</i>	70	30	$\frac{5.444}{5.444}$	
<i>A</i>	<i>a</i>	70	30	$\frac{5.444}{5.444}$	$\frac{5.193}{5.193}$ (2)
<i>B</i>	<i>a</i>	69	31	$\frac{5.193}{5.193}$	
<i>A</i>	<i>a</i>	68	32	$\frac{5.193}{5.193}$	$\frac{5.193}{5.193}$ (3)
<i>B</i>	<i>a</i>	71	29	$\frac{5.193}{5.193}$	
<i>A</i>	<i>a</i>	71	29	$\frac{5.193}{5.193}$	$\frac{5.193}{5.193}$ (4)
<i>B</i>	<i>a</i>	69	31	$\frac{5.193}{5.193}$	
<i>A</i>	<i>a</i>	71	29	$\frac{5.193}{5.193}$	$\frac{5.193}{5.193}$ (5)
<i>B</i>	<i>a</i>	71	29	$\frac{5.193}{5.193}$	
<i>A</i>	<i>a</i>	70	30	$\frac{5.193}{5.193}$	$\frac{5.193}{5.193}$ (6)
<i>B</i>	<i>a</i>	71	29	$\frac{5.193}{5.193}$	
Percentage . . . . .					.18

NOTES.—The spot is colored green on one side by reflection from the paper. The intensity of the color increases with the decrease of the distance from the paper. The other side of the spot is colored pink, which also varies with the distance from the paper, becoming white as the distance increases, and more distinctly pink as the distance decreases. The spot alone is colored. The coloring matter of this paper was found to be arsenic.

## RED PAPER.

Candle.	Position.	Dist. <i>d</i> .	Dist. <i>b</i> + <i>c</i> .	Ratios.	Averages.
<i>A</i>	<i>a</i>	74	26	$\frac{7.31}{7.31}$	$\frac{7.31}{7.31}$ (1)
<i>B</i>	<i>a</i>	73	27	$\frac{7.31}{7.31}$	
<i>A</i>	<i>a</i>	72	28	$\frac{7.31}{7.31}$	$\frac{7.31}{7.31}$ (2)
<i>B</i>	<i>a</i>	73	27	$\frac{7.31}{7.31}$	
<i>A</i>	<i>a</i>	73	27	$\frac{7.31}{7.31}$	$\frac{7.31}{7.31}$ (3)
<i>B</i>	<i>a</i>	72	28	$\frac{7.31}{7.31}$	
<i>A</i>	<i>a</i>	73	27	$\frac{7.31}{7.31}$	$\frac{7.31}{7.31}$ (4)
<i>B</i>	<i>a</i>	73	27	$\frac{7.31}{7.31}$	
<i>A</i>	<i>a</i>	73	27	$\frac{7.31}{7.31}$	$\frac{7.31}{7.31}$ (5)
<i>B</i>	<i>a</i>	72	28	$\frac{7.31}{7.31}$	
<i>A</i>	<i>a</i>	71	29	$\frac{7.31}{7.31}$	$\frac{7.31}{7.31}$ (6)
<i>B</i>	<i>a</i>	72	28	$\frac{7.31}{7.31}$	
Percentage . . . . .					.1406

NOTES.—In the case of red paper the whole of the screen is slightly colored red, but the spot is principally colored. The other side is colored pale green, which deepens as the red grows stronger.

## YELLOW PAPER.

Candle.	Position.	Dist. <i>d</i> .	Dist. <i>b</i> + <i>c</i> .	Ratios.	Averages.
<i>A</i>	<i>a</i>	69	31	$\frac{1}{2.15}$	$\frac{1}{2.15}$ (1)
<i>B</i>	<i>a</i>	70	30	$\frac{1}{2.14}$	
<i>A</i>	<i>a</i>	69	31	$\frac{1}{2.15}$	$\frac{1}{2.15}$ (2)
<i>B</i>	<i>a</i>	70	31	$\frac{1}{2.14}$	
<i>A</i>	<i>a</i>	69	31	$\frac{1}{2.15}$	$\frac{1}{2.15}$ (3)
<i>B</i>	<i>a</i>	67	33	$\frac{1}{2.10}$	
<i>A</i>	<i>a</i>	69	31	$\frac{1}{2.15}$	$\frac{1}{2.15}$ (4)
<i>B</i>	<i>a</i>	68	32	$\frac{1}{2.17}$	
<i>A</i>	<i>a</i>	70	30	$\frac{1}{2.14}$	$\frac{1}{2.15}$ (5)
<i>B</i>	<i>a</i>	66	34	$\frac{1}{2.18}$	
<i>A</i>	<i>a</i>	69	31	$\frac{1}{2.15}$	$\frac{1}{2.15}$ (6)
<i>B</i>	<i>a</i>	68	32	$\frac{1}{2.17}$	
Percentage . . . . .					.2070

NOTES.—The spot is colored yellow on one side, and pearl on the other. The contrast decreases as the distance from the paper increases.

The general results are as follows:—

White . . . . .	.2409
Yellow . . . . .	.2070
Green . . . . .	.1810
Red . . . . .	.1551

## SILVERED MIRROR (FACE).

Candle.	Position.	Dist. <i>d</i> .	Dist. <i>b</i> + <i>c</i> .	Ratios.	Averages.
<i>A</i>	<i>a</i>	51	49	$\frac{1}{1.053}$	$\frac{1}{1.058}$ (1)
<i>B</i>	<i>a</i>	55	45	$\frac{1}{1.15}$	
<i>A</i>	<i>a</i>	52	48	$\frac{1}{1.18}$	$\frac{1}{1.08}$ (2)
<i>B</i>	<i>a</i>	50	50	$\frac{1}{1.00}$	
<i>A</i>	<i>a</i>	55	45	$\frac{1}{1.15}$	$\frac{1}{1.13}$ (3)
<i>B</i>	<i>a</i>	54	46	$\frac{1}{1.17}$	

Candle.	Position.	Dist. <i>d</i> .	Dist. <i>b</i> + <i>c</i> .	Ratios.	Averages.
<i>A</i>	<i>a</i>	52	48	$\frac{1.18}{1.25}$	$\frac{1.18}{1.25}$ (4)
<i>B</i>	<i>a</i>	53	47	$\frac{1.25}{1.25}$	
<i>A</i>	<i>a</i>	51	49	$\frac{1.08}{1.37}$	$\frac{1.25}{1.37}$ (5)
<i>B</i>	<i>a</i>	54	46	$\frac{1.37}{1.37}$	
<i>A</i>	<i>a</i>	54	46	$\frac{1.37}{1.37}$	$\frac{1.37}{1.37}$ (6)
<i>B</i>	<i>a</i>	53	47	$\frac{1.37}{1.37}$	
Percentage . . . . .					.80

NOTES.—The silvered surface of the mirror reflects the yellow color of the candle, while the mercury amalgam mirror gives a more grayish color. Hence, the convenient method of viewing the spot on both sides at once by a mirror, is no longer accurate.

#### SILVERED MIRROR (GLASS SURFACE).

Candle.	Position.	Dist. <i>d</i> .	Dist. <i>b</i> + <i>c</i> .	Ratios.	Averages.
<i>A</i>	<i>a</i>	54	46	$\frac{1.37}{1.37}$	$\frac{1.37}{1.37}$ (1)
<i>B</i>	<i>a</i>	54	46	$\frac{1.37}{1.37}$	
<i>A</i>	<i>a</i>	52	48	$\frac{1.18}{1.37}$	$\frac{1.25}{1.37}$ (2)
<i>B</i>	<i>a</i>	54	46	$\frac{1.37}{1.37}$	
<i>A</i>	<i>a</i>	53	47	$\frac{1.25}{1.37}$	$\frac{1.25}{1.37}$ (3)
<i>B</i>	<i>a</i>	53	47	$\frac{1.25}{1.37}$	
<i>A</i>	<i>a</i>	52	48	$\frac{1.18}{1.48}$	$\frac{1.33}{1.48}$ (4)
<i>B</i>	<i>a</i>	55	45	$\frac{1.48}{1.48}$	
<i>A</i>	<i>a</i>	57	43	$\frac{1.78}{1.08}$	$\frac{1.43}{1.08}$ (5)
<i>B</i>	<i>a</i>	51	49	$\frac{1.08}{1.08}$	
<i>A</i>	<i>a</i>	54	66	$\frac{1.37}{1.08}$	$\frac{1.18}{1.08}$ (6)
<i>B</i>	<i>a</i>	50	50	$\frac{1.08}{1.08}$	
Percentage . . . . .					.775

NOTES.—The back surface of the silvered mirror gives successive reflections.

GENERAL RESULT.—The face of the silvered mirror has been found to reflect more light than any of the six surfaces tried above, and it would probably be found to reflect more than any other surface on account of the superior whiteness of the metal. The double transmission through the glass costs the difference between 80 and 77.5, or 2.5 per cent, disregarding the amount reflected from the



surface of the glass. The silvered mirror used was not perfect, and a perfect silver surface would undoubtedly reflect more, — probably as much as 91 or 92 per cent. Since relative results were desired, but one reflecting angle was used in the above experiments.

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## NO. XX.—EFFECT OF DISTANCE ON APPRECIATION OF COLOR.

By W. H. SCHWARTZ.

Presented Dec. 10, 1879.

HERBERT SPENCER, in his *First Principles of Philosophy*, adduces the following as an instance of heterogeneity in the formation of the Universe: —

“While the yellow stars are found in all parts of the heavens, the red and blue stars are not so; there are wide regions in which both red and blue stars are rare; there are regions in which the red are comparatively abundant.”

Professor Trowbridge suggested to me that the relative distance of the stars, and their relative size, might affect our perception of color, and that a colored star might appear of a faint white or yellow tint on a dark background, if it were distant, compared with a colored star which was at a less distance: in other words, that Herbert Spencer's instance could not be adduced as an evidence of heterogeneity.

I therefore undertook the following investigation.

The solar spectrum having been projected upon a white wall, I covered it by a white screen provided with vertical slits at various distances, and in this way compared my appreciation of the color seen through these slits at various distances. I speedily found that the following experiments with slips of colored paper represented the results which I obtained with the normal colors of the spectrum, and brought out the facts equally well. I therefore abandoned the spectrum, and confined myself to the colored papers.

### RED, GREEN, AND YELLOW.

I first tried strips of red, green, and yellow on a *white background*. The strips were about .0015 meter wide and .025 meter long. They were parallel and about .01 meter apart.

At first, I took red and green strips. At a distance of 12 meters I could tell the difference between the strips because the red was darker than the green, but I could not distinguish the colors at that distance. I could distinguish the colors at about 9 meters. I could tell the direction of the strips at about 16 meters.

I next took green and yellow strips. I could perceive that there was a difference between the colors at 10.5 meters, because the yellow almost blended with the white background, while the green did not look so faint. I could make out the green color at 8 meters, the yellow at 7.5 meters. The direction of the strips could be seen at 14 meters; but no difference could be detected in the colors.

With red and yellow I could perceive that there was a difference at 12 meters, since the red appeared darkest on the white background. I could make out the red color at 9 meters, the yellow at 7.5, and tell the direction of the strips at 16 meters.

All the above were on a *white* background. I then took a *black* background.

#### YELLOW AND GREEN (*narrow strips*).

Could distinguish the colors at 13 meters. Could tell the direction of the strips at 20 meters.

#### RED AND YELLOW (*narrow*).

The yellow is visible at 20 meters, but cannot make out the color at that distance. I can make out the color at 13 meters. Red color is just visible at 8 meters. I can see that there is a strip where the red is, but cannot make out the color at 10 meters.

#### RED AND GREEN (*narrow strips*).

The green can be seen in contrast to the black at 20 meters. The green color can be detected at 13.5 meters. I can make out the red color at 8 meters. The red blends with the black background at 10 meters.

#### YELLOW AND GREEN (*strips twice as wide as those used above*).

I could distinguish a difference of tint at 20 meters; but could make out the colors at 18 meters.

#### RED AND YELLOW (*double width*).

The red color can be made out at 13 meters; but the red strip becomes invisible at 15 meters.

The following measurements were made out of doors :—

Narrow green : color was visible at . . . . .	35 yards.
Narrow yellow : color was visible at . . . . .	24 “
Narrow red : color was visible at . . . . .	16 “

#### DOUBLE WIDTH.

Green color visible at . . . . .	56 yards.
Red “ “ . . . . .	28 “
Yellow “ “ . . . . .	40 “

Red became invisible at 31 yards. I could see the light-colored strips at 75 yards

#### TRIPLE WIDTH.

Green color visible at . . . . .	72 yards.
Red “ “ . . . . .	40 “
Yellow “ “ . . . . .	60 “

The following strips were very carefully measured and cut :—

#### NARROW STRIPS.

Yellow color visible at . . . . .	29 paces.
Green “ “ . . . . .	34 “
Red “ “ . . . . .	18 “

I could see that there were light-colored strips at 48 paces, but could not detect any difference in the colors. The red became invisible at 21 paces.

#### DOUBLE WIDTH.

Yellow color invisible at . . . . .	43 paces.
Green “ “ . . . . .	51 “
Red “ “ . . . . .	23 “

#### TRIPLE WIDTH.

Yellow visible at . . . . .	56 paces.
Green “ . . . . .	67 “
Red “ . . . . .	84 “

By putting these results in close connection, we can compare them to better advantage :—

	Narrow.	Double.	Triple.
Red	16 yards	28 yards	40 yards.
Yellow	24 "	34 "	60 "
Green	35 "	56 "	72 "

These strips were not measured very accurately, but the following were carefully measured :—

	Narrow.	Double.	Triple.
Red	18 paces	23 paces	34 paces.
Yellow	29 "	43 "	56 "
Green	34 "	51 "	67 "

We see from the above table that when the strips are three times as wide, the distance at which they can be seen is just about double.

My conclusions therefore are as follows :—

1. Herbert Spencer's instance cannot be accepted as an evidence of heterogeneity.
2. Distance is an important element in our perception of color. Every one may be said to be color-blind in reference to the stars.
3. The three factors, distance, intensity, and amount of surface from which the illumination proceeds, should be considered in the location of colored signal-lights.
4. Spectrum analysis of very faint stars does not aid us in determining their color, on account of the faintness of the lines.

## NO. XXI.—SIMPLE APPARATUS FOR ILLUSTRATING PERIODIC MOTION.

BY JOHN TROWBRIDGE.

Presented Dec. 10, 1879.

THERE are many ways of showing Lissajous' experiments, and on many accounts the tuning-fork method is the best; but the apparatus is expensive and cannot be readily obtained. The following forms of apparatus can be made by any one at a trifling expense.

### No. 1.—*Graphical Method.*

The apparatus represented in Fig. 1 draws the curves before an audience on the screen, and does not require a vertical lantern. A is

a plate of smoked glass which slides to and fro with a flat board  $m n$ . The latter moves in guides.  $d$  is a brass pointer, which presses against the smoked glass and moves to and fro at right angles to the direction of the board  $m n$ . Two eccentrics connected with the wheels L and E communicate the to and fro motions to the pointer  $d$  and the glass A.

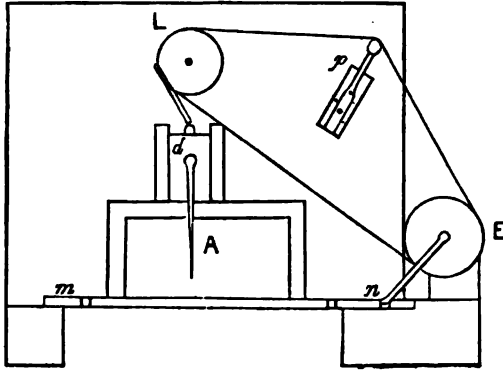


Fig. 1.

This glass is placed in front of the projecting lantern, and the curves of Lissajous are thus drawn on a screen before an audience. By changing the position of the eccentrics, the size of the curves can be modified at pleasure. A pulley,  $p$ , which slides in guides and can be clamped at any point, gives the connecting belt the requisite tension.

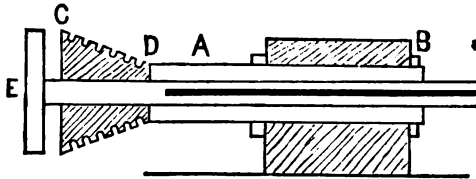


Fig. 2.

The rate of the movement at E can be changed by the device shown in Fig. 2. E is the face of the wheel to which the eccentric is attached. This face is affixed to the end of a slotted shaft which forms the centre of an axle, A B. At one end of this axle is the frustum of a cone, C D, which is provided with grooves for the leather string which serves for a belt to connect the arrangement at E with that at L, Fig. 1. By this arrangement, the same string can be used when the ratio of the wheels is changed; which is done by slipping both the

slotted axle  $AB$  and the slotted shaft connected with  $E$  until they are in position. The string is tightened by means of pulley at  $p$ , Fig. 1.

No. 2. — *Method by Beam of Light.*

Two wires are stretched at right angles to each other, and are maintained in vibration by electro-magnets,  $A$  and  $B$ , placed at the middle of their half-lengths, and by an elastic piece of wire,  $w$  and  $n$ , placed at their middle points. The stretched wires are provided with

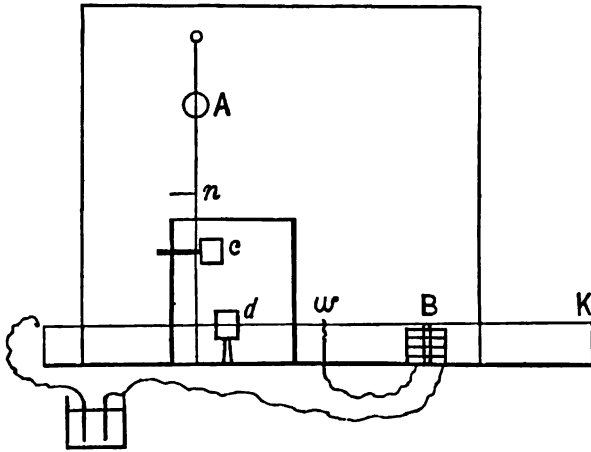


Fig. 8.

mirrors at  $c$  and  $d$ , which are steadied by flexible brass strips attached to the supports upon which the wires are stretched. The horizontal wire is kept in vibration by one battery, and the vertical by another. The process of tuning the wires can be illustrated to an audience by increasing the tension of the horizontal wire by means of a key at  $K$ . When the wires are tuned, a symmetrical and steady figure is produced on the screen, of very large size. The lime light is so placed as to allow the beam of light to fall on the mirror  $d$ , and then on the mirror  $c$ .

## NO. XXII.—ILLUSTRATION OF THE CONSERVATION OF ENERGY.

BY JOHN TROWBRIDGE.

Presented Dec. 10, 1879.

IN the Proceedings of the American Academy, Dec. 11, 1878, can be found a preliminary paper by Mr. W. N. Hill and myself upon the heat developed by the rapid magnetization and demagnetization of iron. The research is still in progress, and we hope to determine how much of the work employed in driving dynamo-electric machines is consumed in heating the iron cores of the generator of electrical currents, and whether this loss of work should turn our attention to forms of generators in which this loss is obviated. It may well be that this loss is not sufficient to counterbalance decided advantages in the present form of such machines.

From my work in this research, I draw the following illustration of the conservation of energy.

Let an induction coil be set in action. In the circuit of the secondary coil place another coil of fine wire. Adjust the terminals of the induction coil so that the spark just passes: then place a core of iron or a bundle of iron wire in the coil which has been included in the secondary circuit. The spark instantly ceases to jump. A portion of the energy of the current in the secondary circuit has been consumed in magnetizing and demagnetizing the iron introduced into the additional coil. The work done in this way is capable of being measured.

It is also evident, that, when a number of telephones are in the same circuit, a part of the energy of the human voice is consumed at each telephone in heating the magnetic cores.

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INVESTIGATIONS ON LIGHT AND HEAT, made and published wholly or in part with appropriation from the RUMFORD FUND.

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## X.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

## XII.—PHOTOMETRIC RESEARCHES.

BY WILLIAM H. PICKERING.

Presented Feb. 11, 1880.

ALTHOUGH many forms of Photometer have been devised within the last hundred years, little has been done towards measuring the brilliancy of our brighter lights, and nothing, so far as I am aware, towards determining the relative intensity of their component colors. With these two objects, and especially the latter one, in view, the following determinations have been made.

The first difficulty encountered was to obtain a steady light, of which the ratio of the component colors should be constant, for use as a standard. Experiments were made using a platinum crucible containing a salt having a high point of fusion. This was to be kept just at the melting point, and thus a constant temperature would be obtained, and consequently a constant light. Several difficulties were encountered, however; among others the cracking of the crucible, owing to the alternate melting and solidification. And moreover the light was not sufficiently brilliant to be wholly satisfactory, so that the idea had to be given up. One interesting result, however, was obtained. Theoretically, the same amount of light would be given out in any direction by a curved surface, as by a flat one; but it was found that at the very edges, the curved surface was noticeably more brilliant than in the middle. That this effect was not due to contrast was shown by placing a brilliant background behind the crucible, when, if contrast produced the effect, it would now have been reversed. But no change in the result was noticeable. Should this result be confirmed, it has an interesting application. The opacity of the atmosphere surrounding the sun has been calculated on the supposition that the theoretical rule is correct; hence, if



incorrect, it is clear that the value so obtained must be somewhat increased.

Several of the artificial lights were next tried. The first one to suggest itself was naturally the standard candle; but a very few experiments sufficed to show that it would not do; and I have since found that of all the lights examined, including the Sun, Lime, Magnesium, and Electric, none was so uncertain in color as the standard candle. After experimenting with several other lights, the standard finally adopted was the gas flame from an Argand burner, using about 5 cu. ft. per hour. A diaphragm .568 cm. in diameter, and having an area of .253 cm.<sup>2</sup> was placed over the most brilliant portion of the flame. A standard was thus obtained which would be almost absolutely constant, in both light and color, during any one set of experiments (usually occupying about an hour), and which I judge from subsequent experiments would vary very little even in the course of a month. The candle-power of the whole flame when burning 5 ft.<sup>3</sup> per hour is about 16.0, that of my standard, .67.

Having obtained a satisfactory light, the next step was to get an instrument by means of which the various lights to be measured could conveniently be compared. For this purpose I use an ordinary double-slit spectroscope, furnished with a grating, having the lines (6480 to the inch) photographed on glass. In front of the slits are placed two right-angled prisms, arranged to reflect the light from opposite directions into the collimator. On looking through the instrument, the two spectra will be seen one above the other, and by means of two sliding metal plates, placed at the focus of the telescope, the spectra may be cut down so that only a narrow vertical strip of each shall be visible.

The standard light is fastened upon a little car, rolling upon a track over a fixed scale, by means of which its distance from the slit is measured. The light to be compared is placed at a known distance on the other side of the slit; the telescope is pointed to some particular color and the standard moved backwards or forwards till the two spectra are of the same brilliancy. The distance is then read off on the scale. In measuring the red and violet ends, it was usually found necessary to place the light to be measured nearer to the slit than for the other colors. The "standard" slit was kept at a constant breadth of .056 mm. through all the experiments, and the light could be moved from it through a distance of from 10 to 60 cms. I found, however, that it was generally better not to place the standard nearer than 15 cms. It will be noticed that the slits are generally kept

quite narrow, as greater accuracy can be attained when the colors are rather faint. Four points in the spectrum were selected for observation, and from these the intervening portions were interpolated. These points were equidistant, and were situated one in the red, one in the yellow, one in the green, and one in the violet; or to speak more accurately, in the neighborhood of the lines C, D, and  $b'$ , and at a point between F and G. They will be designated hereafter by the letters R, Y, G, and V.

I give below my observations on the lime light in full, as a fair example of the accuracy of the instrument, and of the method employed. It will be seen that the first two figures only are of value, the third being used merely for obtaining the mean result. In all my experiments I divide my observations into two sets, made at different times, and the light extinguished between whites; each set is divided into four series, one for each color, and each series consists of at least three, and frequently more observations; thus making at least twenty-four observations on each light. The means of the series are then taken and compared two and two, and their means obtained. From these last the relative brilliancies as compared with the standard are calculated, and plotted as a curve. (See Fig. 1.)

## LIME LIGHT.

Breadth of Slit, .011 mm.

## 1st Set.

Distance to Slit, 1.5 m.

R	Y
21.2	38.8
26.9	39.4
25.9	35.0
3 $\overline{)74.0}$	3 $\overline{)113.2}$
1.5 $\overline{)24.7}$	3 $\overline{)37.7}$
16.4	12.6

Distance to Slit, 8.0 m.

G	V
39.2	21.3
36.4	25.7
34.2	23.4
3 $\overline{)109.8}$	3 $\overline{)70.4}$
3 $\overline{)36.6}$	3 $\overline{)23.5}$
12.2	7.8

## 2d Set.

Distance to Slit, 1.5 m.

R	Y
28.1	42.1
21.3	33.2
30.2	41.1
22.9	45.9
29.6	...
25.3	...
6 $\overline{)157.4}$	4 $\overline{)162.3}$
1.5 $\overline{)26.2}$	3 $\overline{)40.6}$
17.4	13.5

Distance to Slit, 8.0 m.

G	V
36.5	21.2
38.2	25.9
36.2	17.6
...	26.9
...	...
...	...
3 $\overline{)110.9}$	4 $\overline{)91.6}$
3 $\overline{)37.0}$	3 $\overline{)22.9}$
12.3	7.6

*Mean Scale Readings of both Sets.*

R	Y	G	V
16.4	12.6	12.2	7.8
17.4	13.5	12.3	7.6
<u>16.9</u>	<u>13.0</u>	<u>12.2</u>	<u>7.7</u>

*Relative Brilliances.*

R	16.9 <sup>2</sup>	=	28561	Recip.	=	3501	α	59
Y	13.0 <sup>2</sup>	=	16900	"	=	5917	"	100
G	12.2 <sup>2</sup>	=	14884	"	=	6718	"	113
V	7.7 <sup>2</sup>	=	5929	"	=	16866	"	285

After measuring the brightness, I observed the limits of the spectrum under two different brilliancies, and the very curious effect was noticed, that while the red end under the increased illumination advanced considerably, — in the present instance 27', — the violet did not move at all. The same effect is noticeable in all the lights to a greater or less extent, the violet usually moving from 1' to 3'. This is probably accounted for by the fact that the fluids of the eye absorb nearly all the rays of short-wave length, thus cutting off all the spectra at nearly the same place. The position of the red end, on the other hand, depends merely on the intensity of the light.

*Limits of the Spectrum.*

Distance 1.5 m.	Slit 2 mm.	Distance 1.0 m.	Slit .4 mm.
R	V	R	V
41° 55'	37° 23'	42° 24'	37° 24'
56	23	24	24
54	24	18	21
<u>41° 55'</u>	<u>37° 23'</u>	<u>42° 22'</u>	<u>37° 23'</u>

These figures do not represent the deviation of the ray, but merely the numbering on my divided circle. Reducing them to wave lengths we obtain: —

R	V	Slit.	Distance.
709	414	.2 mm.	1.5 m.
740	414	.4 mm.	1.0 m.
<u>31</u>	<u>0</u>		

Advanced.

Next the total brilliancy of the light in candle-powers is measured. In the present case, two determinations were made, one at the end of each set. These measurements were made with a Bunsen pho-

tometer. As the arrangement of the scale in this instance was somewhat complicated, and the form of the observations is well known, I will merely state the results in the two instances as 90 and 84 candle-power. I have since measured the light, and obtained a maximum brilliancy of 231 c. p. And from this, by varying the supply of gas, and the distance of the lime from the burner, the light could be diminished gradually to any extent.

The intrinsic brilliancy is then obtained by placing a diaphragm of known size over the light and remeasuring. As no good standard of intrinsic brilliancy exists, I adopt for the present purpose the light given off by my "standard." This is about .67 of a candle-power at the same distance. When at a maximum, the intrinsic brilliancy of the lime was 121 st. when the total light was 90 c. p. The intrinsic was 54 st.

#### *Probable Error.*

Using a perfectly invariable light, the mean probable error of six observations for the different colors was found to be:—red, 6.7 per cent; yellow, 3.4; green, 2.4; violet, 6.1. These figures may seem rather large, but when we consider that in most of the lights the chief discrepancies are caused not by instrumental errors, but by differences of color, and brilliancy in the lights themselves, we see that it would not be much advantage to have the instrument more accurate than it is; and that if we are to measure the lights at all, we must allow some pretty large variations. Moreover the different lights vary from each other frequently by more than 100 per cent, which leaves room for quite large differences. In fact, we find this to be a subject where the magnitudes are of great range; and accuracy such as we are in the habit of obtaining in other branches is out of the question. The mean probable error of six observations with the Bunsen photometer, on a constant source, varies from .5 per cent under the most favorable circumstances, up to 2 or 3 per cent when less favorable.

#### *Description of Plate I.*

On this plate each broken line represents some particular light. The abscissae denote wave lengths expressed in .00001 of a mm. The ordinates represent the brilliancies of each color, the unit being the brightness of the "standard" for that particular wave length. The standard light is therefore represented by the horizontal line St. As observations were taken only at four particular points, we have no means of knowing the shape of the curves outside of these;

they are therefore prolonged, as horizontal dotted lines, to the farthest limit at which their spectra could be clearly traced. Each curve is designated by a letter, viz.:—St., standard; G, gas; C, candle; L, lime; Mo, moon; E, electric; Mg, magnesium; Su, sun. The positions of the chief solar lines are also marked for convenience of reference. It will be noticed as a curious fact, that the lines  $\alpha$ , C, D, E, a point between F and G and the line H, are almost exactly equidistant; the greatest difference being in the case of C,—.9 mm. on the present scale. B is just midway between  $\alpha$  and C, G midway between the missing line and H.

The following lights were measured in the same manner as the lime light. I shall therefore give only a synopsis of my observations on them.

#### GAS LIGHT.

This is probably the easiest of all the lights to measure, on account of the steadiness and uniformity of its flame. An Argand burner was employed, burning about 5 ft.<sup>3</sup> per hour. It will be seen that it is considerably bluer than the standard, containing 25 per cent more violet. This probably comes from the bluer portions of the flame, which are generally supposed not to give off much light. It has been the custom in constructing gas-burners to suppress these portions as much as possible, but it may be that what a flame thus gains in brilliancy it loses in whiteness.

The following mean readings were obtained:—

R	Y	G	V
14.5	13.1	12.4	9.4
14.0	11.3	11.6	12.4
<u>14.2</u>	<u>12.2</u>	<u>12.0</u>	<u>10.9</u>

#### Brilliances.

74	100	103	125
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#### Limits.

R	V	Sut.	Distance.
690	424	.05 mm.	1.4 m.
726	426	.40 mm.	1.0 m.
<u>86</u>	<u>—2</u>	Advanced.	

Total brilliancy, 16 c. p.

Intrinsic, 1 st.

“Intrinsic” refers in all cases to the brightest part of the flame.

## STANDARD CANDLE.

This was found one of the hardest lights to manage. It was necessary to snuff the wick continually, otherwise the flame would become too brilliant, besides which too much red would be introduced. After a little practice, however, better results were obtained, and when calculated, the curve followed very closely that of the gas-flame. (See Fig. 1.)

*Mean Readings.*

R	Y	G	V
20.5	17.9	16.5	19.2
22.5	19.0	19.6	12.6
<u>21.5</u>	<u>18.4</u>	<u>18.0</u>	<u>15.9</u>

*Brilliances.*

73	100	104	134
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*Limits.*

R	V	Slt.	Distance.
677	432	.2 mm.	1.0 m.
691	429	.4 mm.	.7 m.
<u>14</u>	<u>3</u>	Advanced.	

Total brilliancy, 1 c. p.

Intrinsic, 1 st.

## LIME LIGHT.

This was the next flame measured, and has already been referred to. It is very steady and uniform, and comparatively easy to measure.

## MAGNESIUM LIGHT.

This was obtained by burning two coils of wire simultaneously in a lamp adapted for that purpose. The coils weighed together 56 gms., and burned at the rate of .37 gms. per minute, and would therefore last without renewal for about two hours and a half. Three bright lines were visible in the spectrum, namely D, *b'*, and a line which would come about half way between *b'* and F. These lines fortunately did not come into the field of view in either of my measurements, but would be represented on the curves in Fig. 1. by long vertical lines drawn at these points. The light itself had a very curious appearance when viewed through colored glass. It was the shape of a broad, inverted candle-flame, wavering from side to side, and sometimes splitting in two for nearly its whole length. There seemed to

be no real flame, but a brilliant, striated structure, from which poured up clouds of smoke. The flickering did not annoy me as much as I had expected in my measurements, but was most noticeable in the red. The limits, however, varied considerably, so I took their maximum position.

*Mean Scale Readings.*

R	Y	G	V
473	310	229	100
295	362	222	100
<u>384</u>	<u>386</u>	<u>225</u>	<u>100</u>

The second red was clearly wrong; it was therefore discarded and the first only used.

*Brilliances.*

R	Y	G	V
50	100	223	1,129

The well-known blueness of the flame is clearly accounted for by the great quantity of violet rays present.

*Limits.*

R	V	Slt.	Distance.
695	411	.03 mm.	1.0 m.
715	408	.04 mm.	1.0 m.
<u>20</u>	<u>8</u>	Advanced.	

Total brilliancy, 215 c. p.

Intrinsic, 20.8 st.

**ELECTRIC LIGHT.**

The light was obtained with a Foucault regulator, using 40 pint Grove cells. Six observations were made in each series, instead of three, as in the case of the other lights. The intrinsic brilliancy of both the arc and the carbons was measured. I found the arc to be much fainter, and to vary considerably, while the carbons remained quite constant. If a more powerful current had been used, I think the intrinsic brilliancy of the arc might have increased a little, but the chief difference would have been in its area and that of the ignited carbons.

*Mean Scale Readings.*

R	Y	G	V
192	178	151	68
238	144	155	57
<u>215</u>	<u>161</u>	<u>153</u>	<u>62</u>

The second yellow was here discarded as obviously incorrect.

*Brilliances.*

R	Y	G	V
61	100	121	735

*Limits.*

R	Y	Alt.	Distance.
697	411	.100 mm.	1.5 m.
735	411	.197 mm.	1.0 m.
<hr/> 38	<hr/> 0	Advanced.	

Total brilliancy, 362 c. p.      Intrinsic, carbons, 3141.  
Arc, 645.

## MOONLIGHT.

On account of interruption by clouds, the observations are not quite so satisfactory as some of the preceding ones. Only one series was made on the violet. The moon was just ten days old, and the observations lasted from 9 to 10 P. M. Altitude, 44°.

*Mean Scale Readings.*

R	Y	G	V
440	461	326	242
550	588	415	...
...	565	...	...
<hr/> 495	<hr/> 538	<hr/> 370	<hr/> 242

It would seem as if the last two yellows were too faint. They were therefore discarded.

*Brilliances.*

R	Y	G	V
87	100	155	363

It will be noticed that of all the violet rays sent out by the sun, very few are reflected from the moon (see Fig. 1.), and that the proportion of red rays is quite large, indicating that the surface might partake somewhat of that color, — perhaps like brown lava. And in this case its reddish appearance during total eclipse may not be wholly, as heretofore supposed, due to the absorption of the blue from the solar rays by our atmosphere.

On account of clouds, the limits of the spectrum were not determined.



The total brilliancy was observed several days later, — the day before full moon. Time, 9 P. M., altitude, 20°. Observations were made with both the Bunsen and the Rumford photometers, and are given in full below. Unit, .1 of an inch.

<i>Bunsen.</i>		<i>Rumford.</i>
<i>C. Side.</i>	<i>M. Side.</i>	
883	887	1,097
850	892	1,133
882	913	1,110
956	937	1,115
983	906	1,125
<hr/> 911	<hr/> 907	<hr/> 1,116
		} Mean distance of candle to screen.
<i>Limits.</i>		
1,002	1,043	1,190
790	822	996
<hr/> 896	<hr/> 927	<hr/> 1,093
		} Mean distance of candle to screen.
<i>Difference of Limits.</i>		
212	221	204

*Candle-power at 1 Meter's Distance.*

Bunsen, .187.

Rumford, .124.

The observations with the Bunsen were made from both sides of the disc. In those marked C side, I placed my eye on the side of the candle, in the other it was on the side of the moon. The two means agree very closely; but it was noticed that when the yellow light of the candle passed through the oiled paper, the spot almost completely disappeared; on the other hand, when it was reflected directly from the surface, the setting was much more difficult to make. This difference was very marked, and an examination of the results will show that those made on the side of the moon agree much better than those made on the other side. I shall refer to this point again when I come to the measurements of the sun. On using the Rumford photometer, I was struck with the fact that the measurements did not at all agree with those made by the Bunsen. They agreed with each other, however, more nearly than those made by that instrument, and the difference between their limits was less.

I then set the screen at the mean of the Bunsen readings, but could not convince myself that the shadows were equally dark. The

effect is probably subjective, owing to the great difference of color, and the Bunsen readings are the ones to be relied upon. This would show that the Rumford must never be used to measure lights of different colors, unless the constant error is allowed for. In this case, it amounts to 50 per cent of the whole reading.

#### SUNLIGHT.

My observations on this source were somewhat interfered with by clouds; although on the days available, it was generally clear in the mornings, it nearly always clouded up in the afternoons, which latter were the only times the observations could be made. The first R, Y, and G, were observed at 1 P.M., altitude of sun, 57°, and the rest between 3 and 4.30 P.M., altitude of sun, about 30°.

#### *Mean Scale Readings.*

R	Y	G	V
592	352	276	54
454	325	186	50
...	369	201	88
<u>523</u>	<u>349</u>	<u>221</u>	<u>64</u>

#### *Brilliances.*

R	Y	G	V
45	100	250	2971

The enormous value of the violet as compared with that of the preceding lights is very striking. (See Fig. 1.)

#### *Limits.*

The spectroscope was exposed to the full rays of the sun. The second V, could not be determined on account of the large amount of diffused light admitted.

R.	V	Slit.
728	395	.030 mm.
<u>742</u>	<u>...</u>	.076 mm.
14	...	Advanced.

The total brilliancy of the sun, when at an altitude of 25°, I found to be 64,700 c. p. at 1 meter's distance. Another time, when at 40°, I found it 82,000. That is, it would be equal to about 350,000 full moons. To understand this comparison better, we may add that if the whole visible heavens were turned into one extensive full moon, it would give rather less than one quarter of the light of the sun. The brilliancy has previously been stated at 600,000 full moons.

*Intrinsic Brilliancy 361,000 st.*

These measurements were made with the Buusen photometer, and were all observed from the same side of the disc as the sun. Judging from my measurement of the moon, I had supposed that it would be easier to make my observations from this side, but I was not prepared for the great difference exhibited. From the side of the sun the spot disappeared nearly as perfectly as when measuring a gas flame, particularly if the line of sight was nearly perpendicular to the disc, and the eye was thrown out of focus for it. From the side of the gas, the appearance was that of a bright yellow spot on a bright blue background; and the comparison was almost impossible. The varying brilliancy of different parts of the sun's disc was very marked. I took, as usual, the brightest portion, namely, the centre.

In order to determine the amount of light lost by the *porte lumière*, a reflecting photometer was planned and constructed. A somewhat lengthy series of observations showed that the light lost with the best plate-glass mirrors, 3 mms. in thickness, varied from about 17 to 24 per cent; depending on the angle made by the incident and reflected rays. I believe no wholly satisfactory results have yet been attained, and the measurement has been attempted only once or twice. My results are represented in Fig. 3. The abscissæ represent the angle of the incident and reflected rays. The left-hand ordinates give the per cent of light reflected, the right-hand ones the per cent lost.

*On the Measurement of High Temperatures by the Spectroscope and Photometer.*

It is a fact of common experience, that as we heat a body to higher and higher temperatures, it becomes brighter and at the same time whiter, — in other words, more violet light is given off. Here, then, we have a means of determining qualitatively the temperature of any source. Now if we only knew by what law, either the intrinsic brilliancy, or the violet rays increased with the temperature, and knew at the same time the melting points of some of the metals, we should be able to form some idea of the temperatures, not only of the lime, electric, and magnesium lights, but also of the sun and fixed stars.

Three attempts have been made to determine the temperature of the sun; one by Secchi, supposing the temperature proportional to the radiation of heat; the second founded on Newton's law of cooling; the third dependent upon a numerical exponent, determined from

the experiments of Dulong and Petit. The first two give a temperature of several million degrees, the third about two thousand. I give below the opinions of four well-known modern astronomers, three of them having made the sun their specialty.

Père Secchi says, "As to the absolute value of this temperature, we cannot fix it with certainty. . . . Nevertheless, this temperature must be several million degrees of our thermometer, and capable of maintaining all known substances in a state of vapor."

Prof. Newcomb's views: "For the temperature of the photosphere it seems likely that the lower estimates are more nearly right, but the temperature of the interior must be immensely higher."

Prof. Young's views: "As to the temperature of the sun's surface, I have no settled opinion, except that I think it must be much higher than that of the carbon points of the electric light. . . . The estimates dependent on Newton's law seem to me manifestly wrong and exaggerated; on the other hand, the low estimates of the French physicists seem to me hardly more trustworthy."

Prof. Langley says, "The temperature of the sun is, in my view, necessarily much greater than that assigned by the numerous physicists, who maintain it to be comparable with that obtainable in the laboratory furnace; but we cannot assign any upper limit to it, until physics has advanced beyond its present merely empirical rules connecting emission and temperature."

Now we know from the experiments of Prof. Draper and others, that as the temperature rises, the light increases *much* more rapidly than the heat; and let us suppose that this law holds good up to the temperature of the sun. Since we do not know any terrestrial high temperature with certainty, great accuracy is manifestly out of the question. Heated bodies begin to give out light at about  $500^{\circ}\text{C}$ ; silver melts at about  $1,000^{\circ}\text{C}$ . Many determinations of the melting point of platinum have been made, which give it in the neighborhood of  $2,000^{\circ}\text{C}$ . The temperature of the electric arc has been estimated at between  $3,000^{\circ}$  and  $4,000^{\circ}\text{C}$ , — let us say,  $3,500^{\circ}$ . The intrinsic brilliancy of the carbons of the electric light we found to be 3,141, that of the sun, 86,100. This was determined at an altitude of  $25^{\circ}$ , — let us suppose our atmosphere removed and double it, obtaining 72,000. It has been shown by my brother, Prof. Pickering, that only about one fourth the light from the centre of the sun's disc reached the earth. We will therefore multiply its brilliancy by 4, obtaining 288,000. Divide by the intrinsic brilliancy of the electric light (3,141), and we find the sun to be 90 times as brilliant. Then

the heat can certainly not be more than 90 times as great, and is probably much less. Since bodies begin to glow at about  $500^{\circ}\text{C}$ , the following equation will determine the solar temperature:—

$$90 (3,500 - 500) + 500 = 270,500^{\circ}\text{C}.$$

Our upper limit would thus be brought down from several millions of degrees to about  $270,000^{\circ}\text{C}$ .

Now as to the lower limit. The temperature of the hottest blast furnaces is about  $2,000^{\circ}\text{C}$ , or about that of the lime light. That the sun is far hotter than this, or even the electric light, is manifest by an examination of the curves in Fig. 1. Let us take  $8,000^{\circ}$  as a lower limit, as found by inspection. On observing the spectrum of melted silver, I found that it just about reached to the violet rays. Also the heat of the oxyhydrogen jet is approximately the melting point of platinum. Let us now construct a curve, Fig. 2., in which the unit of abscissas shall be  $1,000^{\circ}\text{C}$ , and the ordinates the same as in Fig. 1., but on a different scale. Then the point Si will represent the position of melted silver, L the lime-light or melted platinum, and E the electric light. We find that these three points all lie in a straight line. Then if the temperatures we adopted were correct, this would give us a very simple empirical law, viz:— *The temperature is always proportional to some function of the ratio of any two assumed wave-lengths. For artificial sources, for the wave-lengths 585 and 455, it varies directly as this ratio.* Supposing this law to be uniformly true, the temperature of the sun would be  $11,000^{\circ}\text{C}$ . But from a comparison of the experiments of Dr. Vogel, and Prof. Pickering, it would seem that the sun's atmosphere absorbs a much larger proportion of the violet rays, than it does of the yellow. We know this to be the case with our atmosphere, therefore let us double the temperature (and this coefficient cannot be very far out of the way), and we may therefore conclude that the temperature of the sun is approximately  $22,000^{\circ}\text{C}$ .

This amount is, we notice, considerably within the limits we had previously set.

Upon this principle, the temperature of the magnesium light, perhaps the highest terrestrial temperature we have yet attained, would be  $4,900^{\circ}\text{C}$ , as shown by Fig. 2. Its small intrinsic brilliancy is readily accounted for, when we recollect that this depends on the area of the ignited solid matter, and that this, in the case of the magnesium light, consists almost wholly of the impalpable oxide which forms the smoke.

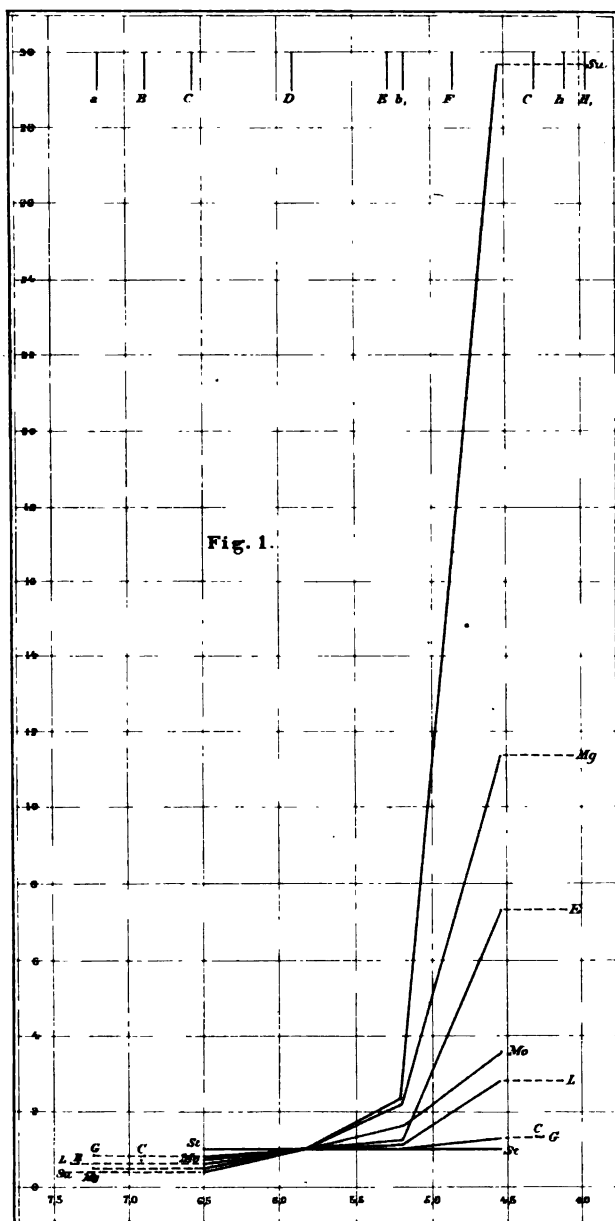
It is perhaps unnecessary to add, that the above-mentioned law of the increase of the violet rays is inapplicable to flames like the blue part of the gas, where no solid matter is introduced. It probably applies in a modified form, to lime flames, as witness the disappearance of the blue line in the strontium spectrum, at low temperatures.

*Second Estimation of the Sun's Temperature.*

Below is given a table showing the total and intrinsic brilliancies, as well as the temperatures, of the several sources referred to in this article.

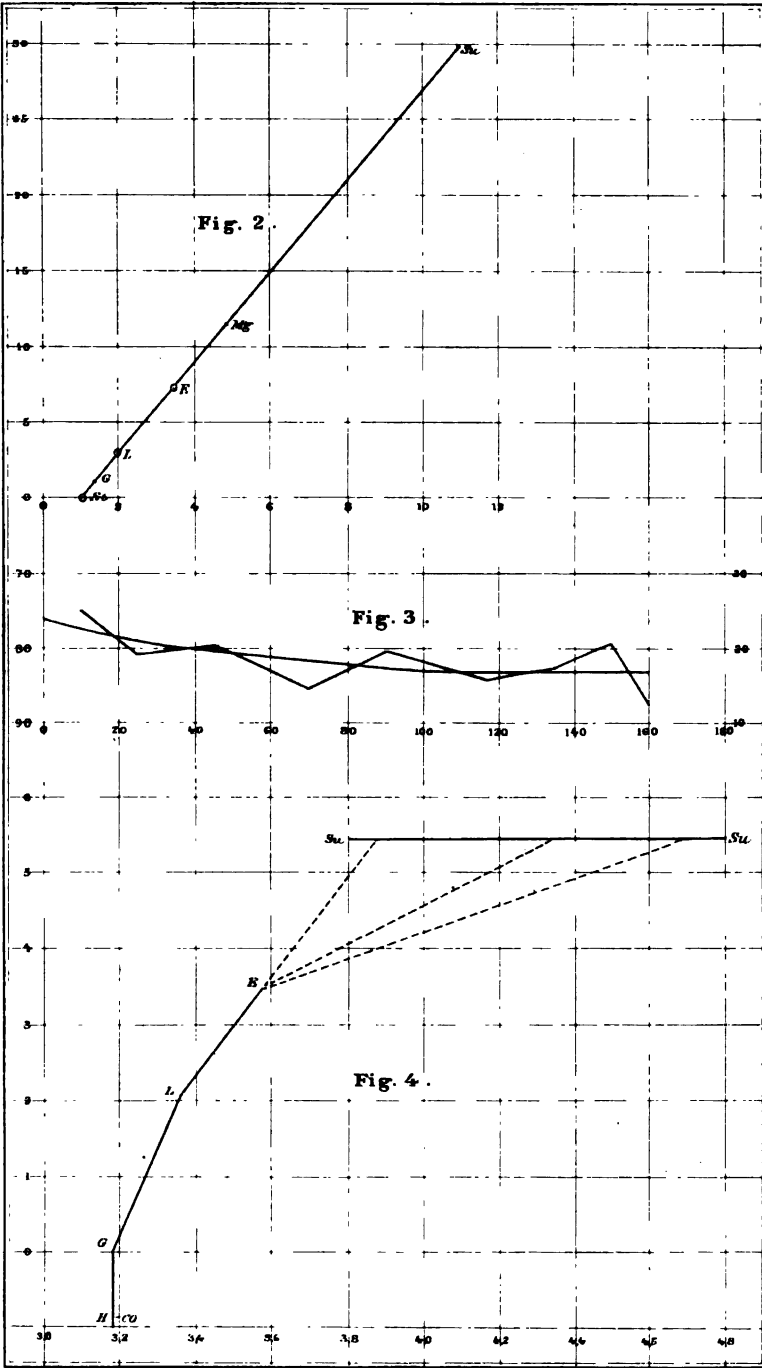
Source of Light.	Total Brilliancy.	Intrinsic Brilliancy.	Tempera- ture.	Absolute Tem.	Log. Int. Bril.	Log. Abs. Temp.
Heated Body .....	0	0	500	800	— $\infty$	2.93
Melted Silver .....	.....	.....	1,000	.....	.....	.....
Gas or Candle.....	16...1	1	1,200	1,500	0.00	8.18
Lime light.....	231	121	2,000	2,800	2.08	8.86
Electric light.....	862	8,141	8,600	8,800	8.50	8.68
Magnesium light..	215	21	4,900	.....	.....	.....
Sun (observed)....	82,000	86,100	.....	.....	.....	.....
Sun (corrected)....	.....	288,000	22,000	22,800	5.46	4.84
Lower limit.....	.....	.....	.....	7,600	.....	8.88
Upper limit.....	.....	.....	.....	50,000	.....	4.70

Let us now construct a curve with the figures of the seventh column as abscissae and the sixth as ordinates. The gas flame, although not properly speaking an incandescent body, may still be used to fix a lower limit to our curve at that point. This curve is represented in Fig. 4. The horizontal line, Su, represents the corrected intrinsic brilliancy of the sun. It will be seen that the curve cannot intersect it to the left of the left-hand dotted line, and is not likely, so far as one can judge from the form of the curve, to cross it to the right of the right-hand one. These would give to the sun limiting temperatures of 7,600° and 50,000° C. The middle dotted line corresponds to the temperature we previously found of 22,000° C.











## XI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.

## THE ATOMIC WEIGHT OF ANTIMONY.

## PRELIMINARY NOTICE OF ADDITIONAL EXPERIMENTS.

BY JOSIAH P. COOKE.

*Erving Professor of Chemistry and Mineralogy.*

Presented March 10, 1880.

IN our previous paper on this subject,\* we gave our reasons for the opinion, since fully confirmed, that the bromide of antimony is the most suitable compound of this element, as yet known, for determining its atomic weight; and the results of fifteen analyses of five different preparations of the bromide were published, which gave for the atomic weight in question the mean value 120.00 with an extreme variation between 119.4 and 120.4 for all the fifteen analyses, and between 119.6 and 120.3 for the six determinations in which we placed most confidence. The antimonious bromide used in these determinations was purified first by fractional distillation, and secondly by crystallization from a solution in sulphide of carbon. In the crystallized product thus obtained, the bromine was determined gravimetrically as bromide of silver in the usual way. Although it seemed at the time that the results were as accordant as the analytical process would yield under the unfavorable conditions, which the presence of a large amount of tartaric acid in the solution of the bromide of antimony necessarily involved; yet it was obvious that the agreement was far from that which was desirable in the determination of an atomic weight, and our chief confidence in the accuracy of the mean value —

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\* These Proceedings, Vol. XII. page 1.

independently of its remarkable agreement with previous results — was based on the fact that the known sources of error tended to balance each other. Hence our conclusions were stated with great caution, and the hope was expressed that after a more thorough investigation of the subject we might be able “to return to the problem with such definite knowledge of the relations involved as will enable us to obtain at once more sharp and decisive results than are now possible.” Unfortunately this investigation has been delayed by causes beyond our control.

In our previous paper, we described a simple apparatus which we devised for subliming iodide of antimony; and in a note to the paper we stated that we were applying the same process to the preparation of the bromide of antimony, and that it promised excellent results. Our expectations in this respect have been fully realized, and the product leaves nothing to be desired either as regards the beauty or the constancy of the preparation. The fine acicular crystals are perfectly colorless, and have a most brilliant silky lustré. With ordinary precautions they can be kept indefinitely without change, and it is easy therefore to determine the weight of the material analyzed to the tenth of a milligramme.

We have carefully studied the causes of error involved in the analytical process of determining bromine in an aqueous solution of bromide of antimony and tartaric acid by the usual gravimetric method. These causes we propose to discuss in a future more extended paper. In this preliminary notice, we have only space to state that we have satisfied ourselves that the small differences between the results previously obtained arose wholly from the analytical process, and not from any want of constancy in the material analyzed; and further that these sources of error are to a very great extent under control. Moreover, we have found that the volumetric determination of bromine by silver was not materially affected, if at all, by the same causes. We have thus been led to devise a mode of testing the atomic weight of antimony, which, while it has all the advantages of the gravimetric method previously employed, is free from its sources of error.

If the atomic weight of antimony were 122.00, it would require 1.7900 grammes of pure silver to precipitate the bromine from a solution of 2.0000 grammes of antimony bromide, while if the atomic weight of antimony were 120.00 it would require 1.8000 grammes of silver. Now it is easy to estimate volumetrically  $\frac{1}{100}$  of this difference with great certainty. We therefore prepared with great care

a button of *pure* metallic silver, which we annealed and rolled out to a thin ribbon. We then weighed out from two to four grammes of bromide of antimony, prepared by sublimation as described above, and dissolved this salt in an aqueous solution of tartaric acid, which we then transferred to a litre flask and diluted to about 500 cubic centimetres. We next very accurately weighed out a quantity of silver slightly less than that which calculation showed was required for complete precipitation. This silver was dissolved in nitric acid, and the solution having been evaporated to dryness over a water bath, the silver salt was washed into the flask containing the bromide of antimony. As soon as the supernatant liquid had cleared, the small additional amount of a normal silver solution required to produce complete precipitation was run in from a burette, and measured with the usual precautions. We used no extraneous indicator, because it was important not to introduce any possibly new disturbing element into the experiment, and in the titration of bromine with silver the normal and familiar phenomena, which mark the close of the process, furnish a very sharp indication. The details of one of the determinations were as follows:—

The weight of the bromide of antimony used amounted to 2.5032 grammes. To precipitate the bromine from the solution of this material 2.2404 grammes of silver would be required if  $Sb = 122.00$  and 2.2529 if  $Sb = 120.00$ . We weighed out, with as much accuracy as if we were adjusting a weight, the smaller of these two quantities of metallic silver, and after dissolving the pure metal in pure nitric acid, evaporating the solution to dryness and redissolving in water, we added at once the whole of this silver solution to the litre flask containing the solution of bromide of antimony, in the manner described above. It was then found that  $12\frac{4}{10}$  cubic centimetres of a normal silver solution (one gramme of silver to the litre) were required to complete the precipitation. It will be seen that the weights of the bromide of antimony and silver used could be thus determined with the most absolute precision, and we have the greatest confidence in these values to the  $\frac{1}{10}$  of a milligramme. Moreover, it will be noticed that the volumetric method is only used to estimate the difference in the atomic weight which has been in question, and that if the method were only accurate to the  $\frac{1}{10}$  of the quantity to be measured it would give us the value of the atomic weight within  $\frac{1}{20}$  of a unit; while if, as we had reason to believe, the process was accurate within one per cent, it would fix the atomic weight within  $\frac{1}{200}$  of a unit.

By the method just described, the following results were obtained. The letters *a* and *b* indicate different preparations.

Wt. of Sb Br <sub>3</sub> taken.	Total Wt. of Ag used.	Per Cent of Br Ag = 108 Br = 80.	Corresponding value of Sb.
<i>a</i> 1. 2.5032	2.2528	66.6643	120.01
<i>a</i> 2. 2.0567	1.8509	66.6620	120.02
<i>a</i> 3. 2.6512	2.3860	66.6644	120.01
<i>b</i> 4. 3.3053	2.9749	66.6696	119.98
<i>b</i> 5. 2.7495	2.4745	66.6653	120.01
Mean value,		66.6651	120.01
Mean value of fifteen gravimetric de- terminations previously published,		66.6665	
Theory Sb. 120 requires		66.6666	
„ Sb. 122 „		66.2983	

In order still further to control the work, we collected the bromide of silver formed in the last two determinations, washing the precipitate with the precautions which experience had shown to be necessary, and determining its weight, first, after drying at 150° C., and, secondly, after heating to incipient fusion. In *b* 6 there was a loss of  $\frac{1}{10}$  of a milligramme; in *b* 7 a loss of  $\frac{1}{10}$  of a milligramme only at the second weighing. This is an absolute proof that there could be no sensible occlusion of any tartaric acid or any tartrate by these precipitates, and, as stated in our original paper, the same test was frequently applied, although not always, in our previous determinations. It is also evident that these last experiments give us two essentially distinct determinations of the atomic weight, although the materials employed were identical with those of *b* 4 and *b* 5.

Wt. of Sb Br <sub>3</sub> taken.	Wt. of Ag Br determined.	Per cent of Bromine Ag = 108 Br = 80.	Corresponding value of Sb.
<i>b</i> 6. 3.3053	5.1782	66.665	120.01
<i>b</i> 7. 2.7495	4.3076	66.667	120.00
Mean value,		66.666	120.00

Lastly, it is obvious that these gravimetric determinations, taken in connection with the corresponding volumetric results, give us the most conclusive evidence of the purity, both of the metallic silver used, and

also of the bromine in the bromide of antimony, which is the basis of this atomic weight investigation. By comparing *b* 6 and *b* 7 with *b* 4 and *b* 5 respectively, we obtain the following data :—

1. 2.9749 gram. of silver gave 5.1782 gram. bromide of silver.
2. 2.4745       "       "       "       4.3076       "       "       "

Hence it follows that, as shown by these experiments, the proportions of the silver to the bromine were respectively :—

	1.	108.00	Silver to	79.99	Bromine.
	2.	108.00	" "	<u>80.01</u>	"
Mean value,		<u>108.00</u>	" "	<u>80.00</u>	"

This is the ratio of the atomic weight of silver to that of bromine, and corresponds to the second decimal place with the determinations of Stas as well as with those of Dumas.

In conclusion it gives us pleasure to express our obligations to Mr. G. De N. Hough and Mr. G. M. Hyams, two students of this laboratory, who have greatly aided us in the experimental work of this investigation.

## XII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.

## ON THE ETHERS OF URIC ACID.

## SECOND PAPER.

## DIMETHYLURIC ACID.

BY H. B. HILL AND C. F. MABERY.

Presented April 14, 1880.

DIMETHYLURIC acid is formed when diplumbic urate is heated with methyl iodide according to the general method which one of us has already described\* for making the monomethyl compound. The preparation of considerable quantities of pure substance by this method is, however, a matter of some difficulty, and we have found that a close attention to details is necessary to insure success.

The diplumbic urate which we used at first was made according to the directions of Allan and Bensch,† by precipitating a boiling solution of plumbic nitrate with dipotassic urate purified by alcohol. Although we heated this lead salt with an excess of methyl iodide at various temperatures (100° to 170°) for different lengths of time (five to ninety hours), we could not succeed in obtaining from it a product which did not contain quite a large percentage of the monomethyl ether. We therefore attempted to effect the separation of the monomethyl and dimethyl compounds by fractional crystallization, or by methods based upon differences in the behavior of their salts; but we were unable to find a method which was at all satisfactory, and, after many experiments, convinced ourselves that it was necessary to obtain from the first a product essentially free from the monomethyl compound.

After a long series of experiments which need not be described in detail, we found that such a product could be obtained from a lead

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\* These Proceedings, Vol. XII. p. 27.

† Ann. Chem. u. Pharm., lxx. 191.



salt made by precipitating with the diplumbic urate a small amount of plumbic hydrate. We have made no experiments to show how small this quantity of plumbic hydrate can be made with safety, as it seemed a matter of little importance. In preparing the lead salt we dissolved uric acid in a potassic hydrate solution of known strength, using twenty per cent more potassic hydrate than was theoretically required to form the dipotassic urate, and poured this alkaline solution into a boiling dilute solution of plumbic nitrate. After washing the bulky precipitate with hot water we usually washed with alcohol, and finally with a little ether; partly to facilitate the drying, and partly because the lead salt was in this way obtained in a much more compact and convenient form. After drying at  $100^{\circ}$  the salt was well powdered and dried at  $160^{\circ}$ .

In order to insure complete decomposition of the lead salt, which evidently is essential to prevent the formation of monomethyluric acid, we have found it necessary to take a slight excess of methyl iodide, to dilute it with an equal weight of ether, and, after mixing thoroughly with the lead salt, to heat for twenty hours at  $165^{\circ}$ . We also have found it advantageous to allow the tube to cool after heating for twelve to fifteen hours, and to mix the contents thoroughly by shaking before heating further.

After distilling off the ether and the slight excess of methyl iodide, the solid product of the reaction is extracted with boiling water, and the lead precipitated by hydric sulphide. The solution filtered boiling hot deposits on cooling crystals of dimethyluric acid which may be purified by recrystallization from hot water. In this way we have obtained about fifty per cent of the theoretical yield of well crystallized product apparently pure. Since monomethyl and dimethyluric acids differ in the amount of carbon they contain only by 3.29 per cent, it is evident that the absolute purity of our product could not be determined by analysis.

Dimethyluric acid crystallizes usually in slender oblique prisms, often concentrically grouped, which contain a molecule of crystal water. From saturated solutions where crystallization takes place at a high temperature we have not unfrequently obtained small, compact, pointed prisms, which contain less water and very possibly are anhydrous. The behavior of both of these forms to polarized light shows that they belong to one of the oblique systems. The acid begins to turn brown when heated to about  $340^{\circ}$ ; at higher temperatures it melts, with decomposition and partial sublimation. It is quite soluble in boiling water, sparingly soluble in cold water, still less so in

alcohol, and insoluble in ether. Concentrated sulphuric and hydrochloric acids dissolve it readily, and deposit the greater portion upon dilution.

The slender oblique prisms in which methyluric acid ordinarily crystallizes contain one molecule of water when dried in vacuo over sulphuric acid.

0.6067 gr. lost at  $160^{\circ}$  0.0511 gr.  $H_2O$  = 8.49%.

The formula  $C_5H_2(CH_3)_2N_4O_3 \cdot H_2O$  requires 8.41%.

The crystals of the second form were obtained for analysis by evaporating a saturated solution of the acid upon the water-bath, and filtering hot. Although our determinations agree closely with the amount required for a half-molecule of water, it is not impossible that the loss in weight is due to hygroscopic moisture, as was the case with the monomethyl acid.

I. 0.4547 gr. substance dried in vacuo lost at  $160^{\circ}$  0.0196 gr.  $H_2O$  = 4.31%.

II. 0.2651 gr. lost 0.0114 gr.  $H_2O$  = 4.30%.

The formula  $C_5H_2(CH_3)_2N_4O_3 \cdot \frac{1}{2}H_2O$  requires 4.39%.

The composition of the substance dried at  $160^{\circ}$  was determined by the following analyses:—

- I. 0.2747 gr. gave 0.1097 gr.  $H_2O$  and 0.4291 gr.  $CO_2$ .
- II. 0.2022 gr. gave 0.0789 gr.  $H_2O$  and 0.3167 gr.  $CO_2$ .
- III. 0.1393 gr. gave 0.0557 gr.  $H_2O$  and 0.2185 gr.  $CO_2$ .
- IV. 0.3521 gr. gave 86 cc. nitrogen at  $16^{\circ}$  and 756.5 mm. pressure.

	Calculated for $C_5H_2(CH_3)_2N_4O_3$	1.	Found. 2.	3.	4.
C	42.85	42.60	42.72	42.78	
H	4.08	4.44	4.34	4.44	
N	28.57				28.21

The solubility in boiling water was determined by filtering a boiling saturated solution through a hot-water filter into weighed flasks. After cooling, the flasks were weighed, the contents transferred to platinum dishes, evaporated to dryness, and the residue dried at  $165^{\circ}$ .

I. 54.2110 gr. solution left 0.2043 gr. residue.

II. 57.8596 gr. solution left 0.2940 gr. residue.

The boiling saturated solution contains the following percentages:—

1.	2.
0.5152	0.5081

To determine the solubility in cold water a hot solution was kept at 20° for four hours with occasional stirring. The solution was then filtered into weighed platinum crucibles, evaporated to dryness, and the residue heated at 160°.

- I. 35.6147 gr. solution left 0.0189 gr. residue.
- II. 25.2221 gr. solution left 0.0134 gr. residue.
- III. 21.9260 gr. solution left 0.0116 gr. residue.

The solution saturated at 20° contained in percentages: —

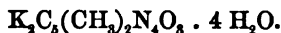
1.	2.	3.
0.0531	0.0532	0.0529

Taking the mean of these results dimethyluric acid requires for solution 195.2 parts boiling water and 1885.3 parts of water at 20°.

An aqueous solution has a slight acid reaction, and decomposes carbonates on heating. A solution in sodic or potassic hydrate is not precipitated by carbonic dioxide. From concentrated cold solutions it is precipitated by stronger acids in a gelatinous form; from more dilute solutions it separates in crystals.

#### SALTS OF DIMETHYLURIC ACID.

##### *Dipotassic dimethylurate.*



Dimethyluric acid was dissolved in an excess of a dilute solution of potassic hydrate, the clear solution boiled for several minutes, and about ten volumes of alcohol added. The crystalline precipitate, which separated on standing, was filtered off rapidly by the pump, washed with alcohol, and dried in vacuo over sulphuric acid and potassic hydrate. This salt crystallizes in fine silky needles, which are very soluble in water. It absorbs carbonic dioxide very rapidly from the air, probably forming the monopotassic salt.

To determine the water of crystallization the salt was heated in a current of dry air, free from carbonic dioxide.

0.8079 gr. salt dried in vacuo gave 0.1662 gr. $\text{H}_2\text{O}$	=	20.57%
Calculated for $\text{K}_2\text{C}_5(\text{CH}_3)_2\text{N}_4\text{O}_8 \cdot 4 \text{H}_2\text{O}$	. . .	20.92%
0.3198 gr. anhydrous salt gave 0.1766 gr. $\text{KCl} \cdot \text{K}$	=	28.95%
Calculated for $\text{K}_2\text{C}_5(\text{CH}_3)_2\text{N}_4\text{O}_8$	. . . . .	28.73%

*Monopotassic dimethylurate.*

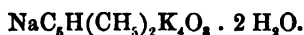
Potassic carbonate, in slight excess of the theoretical amount, is added to the acid suspended in boiling water. The solution is boiled for some time, and the salt precipitated by adding about ten volumes of alcohol. It is then filtered, washed with alcohol, and dried in vacuo over sulphuric acid. The salt crystallizes in branching needles, which are quite soluble in water.

0.2540 gr. salt dried in vacuo gave 0.0278 gr. $\text{H}_2\text{O}$	=	10.94%
Calculated for $\text{KC}_5\text{H}(\text{CH}_3)_2\text{N}_4\text{O}_8 \cdot 1\frac{1}{2} \text{H}_2\text{O}$	.	10.35%
0.2180 gr. anhydrous salt gave 0.0702 gr. $\text{KCl} \cdot \text{K}$	=	16.88%
Calculated for $\text{KC}_5\text{H}(\text{CH}_3)_2\text{N}_4\text{O}_8$	.	16.70%

*Disodic dimethylurate.*

This salt is precipitated from a sodic hydrate solution of the acid by alcohol in the same way as the dipotassic salt. It crystallizes in needles much larger than those of the corresponding potassic salt.

0.3064 gr. salt dried in vacuo gave 0.0780 gr. $\text{H}_2\text{O}$	=	25.46%
Calculated for $\text{Na}_2\text{C}_5(\text{CH}_3)_2\text{N}_4\text{O}_8 \cdot 4\frac{1}{2} \text{H}_2\text{O}$	.	25.23%
0.2234 gr. anhydrous salt gave 0.1074 gr. $\text{NaCl} \cdot \text{Na}$	=	18.91%
Calculated for $\text{Na}_2\text{C}_5(\text{CH}_3)_2\text{N}_4\text{O}_8$	.	19.17%

*Monosodic dimethylurate.*

This salt was made in the same way as the monopotassic salt. It forms microscopic needles which are more soluble in water than the potassic salt.

0.5327 gr. salt dried in vacuo gave 0.0798 gr. $\text{H}_2\text{O}$	=	14.98%
Calculated for $\text{NaC}_5\text{H}(\text{CH}_3)_2\text{N}_4\text{O}_8 \cdot 2 \text{H}_2\text{O}$	.	14.18%
0.3069 gr. anhydrous salt gave 0.0638 gr. $\text{NaCl} \cdot \text{Na}$	=	10.17%
Calculated for $\text{NaC}_5\text{H}(\text{CH}_3)_2\text{N}_4\text{O}_8$	.	10.54%

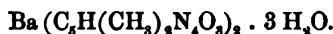
*Dibasic dimethylurate.*

Dimethyluric acid was dissolved in as little boiling water as possible, a solution of baric hydrate added in slight excess of the amount

theoretically required, and the solution boiled. The salt separated as the solution cooled, and was purified by recrystallization from hot water. It was filtered rapidly and dried in vacuo over sulphuric acid and potassic hydrate. The salt is quite soluble in hot, but slightly soluble in cold water. When cooled rapidly, it forms a jelly-like mass; but when cooled slowly, it crystallizes in flat, transparent prisms.

0.2177 gr. salt dried in vacuo gave 0.0307 gr. $\text{H}_2\text{O}$	= 14.10%
Calculated for $\text{BaC}_5(\text{CH}_3)_2\text{N}_4\text{O}_3 \cdot 3 \text{H}_2\text{O}$	. . . 14.03%
0.1875 gr. anhydrous salt gave 0.1335 gr. $\text{BaSO}_4$	. Ba = 41.86%
Calculated for $\text{BaC}_5(\text{CH}_3)_2\text{N}_4\text{O}_3$	. . . . . 41.89%

*Monobasic dimethylurate.*



This salt was made by boiling an aqueous solution of the acid with baric carbonate, filtering, and precipitating the filtrate with alcohol.

0.3661 gr. salt dried in vacuo gave 0.0342 gr. $\text{H}_2\text{O}$	= 9.34%
Calculated for $\text{Ba}(\text{C}_5\text{H}(\text{CH}_3)_2\text{N}_4\text{O}_3)_2 \cdot 3 \text{H}_2\text{O}$	. . . 9.29%
0.3350 gr. anhydrous salt gave 0.1491 gr. $\text{BaSO}_4$	. Ba = 26.17%
Calculated for $\text{Ba}(\text{C}_5\text{H}(\text{CH}_3)_2\text{N}_4\text{O}_3)_2$	. . . . . 25.99%

Further study of the salts of dimethyluric acid seemed to us of no immediate importance, since the results we had reached served to establish beyond all doubt its dibasic character.

*Action of Hydrochloric Acid.*

Dimethyluric acid, when heated with concentrated hydrochloric acid, is completely decomposed, giving products perfectly analogous to those described by Strecker\* as resulting from the decomposition of uric acid, and qualitatively identical with those obtained under the same conditions from methyluric acid.

The dimethyluric acid was heated for several hours with hydrochloric acid saturated at  $0^\circ$  to  $170^\circ$ . The liquid from the tubes, which showed great pressure on opening, was evaporated to dryness on the water-bath, the residue dissolved in water and distilled with plumbic hydrate in a current of steam as long as the distillate gave an alkaline reaction. The distillate was caught in hydrochloric acid, evap-

\* Ann. Chem. u. Pharm., cxlvi. 142; Zeitschr. für Chemie, 1868, p. 215.

orated to dryness on the water-bath, and the residue treated with a mixture of absolute alcohol and ether. Ammonic chloride was left undissolved, while in solution was a salt which gave qualitative tests characteristic of the monamines. The platinum salt, recrystallized from water, gave on analysis:—

0.5421 gr. left on ignition 0.2261 gr. platinum.

	Calculated for $(CH_3NH_2)_2PtCl_4$ .	Found.
Pt	41.61	41.75

In order to find the relative amounts of ammonia and methylamine which were formed in this reaction, we determined the percentage of chlorine in the saline residue as obtained by distillation with plumbic hydrate. The residue of chlorides was dried at  $100^\circ$  and the chlorine precipitated by argentic nitrate.

0.6365 gr. mixed chlorides gave 1.4681 gr.  $AgCl$ .  $Cl_2 = 57.07\%$

Calculated for 2 molecules methylamine chloride

and 1 molecule ammonic chloride . . . . = 56.50%

Two molecules of methylamine are therefore formed in the reaction and one molecule of ammonia.

The liquid remaining in the flask, after the distillation, was filtered hot, the lead precipitated as sulphide, and the filtered solution concentrated. On long standing crystals of glyocol separated, which, for identification, were converted into the copper salt by boiling with freshly precipitated cupric oxide, and precipitating the filtered solution with alcohol.

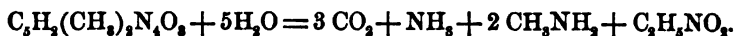
0.4757 gr. copper salt lost at  $185^\circ$  0.0391 gr.  $H_2O$ .

	Calculated for $(C_2H_4NO)_2Cu \cdot H_2O$	Found.
$H_2O$	7.85	8.22

0.4291 gr. anhydrous salt left on ignition 0.1611 gr.  $CuO$ .

	Calculated for $(C_2H_4NO)_2Cu$ .	Found.
$CuO$	37.55	37.54

The reaction may therefore be written:—



#### *Oxidation of Methyluric Acid.*

By the oxidation of dimethyluric acid with nitric acid we were unable to obtain a crystalline product. Since the crystalline amalic acid would undoubtedly have been formed had the two methyl radicals been attached to the same urea residue, we concluded that our sirupy oxidation product contained methylalloxan, and for its iden-

tification converted it at once into the calcic methylalloxanate. We followed closely the method which one of us had already described,\* and found to give constant results. Dimethyluric acid was dissolved in the smallest possible quantity of nitric acid of sp. gr. 1.42, the solution diluted with water, and the excess of acid neutralized with calcic carbonate in the cold. After the solution was freed as nearly as possible from carbonic dioxide, by allowing it to stand for some time in vacuo, it was largely diluted with alcohol, filtered, and the calcic methylalloxanate precipitated by the cautious addition of ammonia. The carbon and hydrogen were estimated in this salt dried at 100° by a combustion in a stream of oxygen, the calcium by ignition with sulphuric acid.

- I. 0.2334 gr. substance gave 0.2103 gr.  $\text{CO}_2$ , 0.0439 gr.  $\text{H}_2\text{O}$ , and 0.0921 gr. residue. This residue gave 0.1489 gr.  $\text{CaSO}_4$ , equivalent to 0.0611 gr. calcic oxide. The residue, therefore, contained 0.0311 gr.  $\text{CO}_2$ .  
 II. 0.2172 gr. gave 0.1401 gr.  $\text{CaSO}_4$ .  
 III. 0.2268 gr. gave 0.1448 gr.  $\text{CaSO}_4$ .

	Calculated for $\text{C}_2\text{H}(\text{CH}_2)_2 \cdot \text{N}_2\text{O}_6\text{Ca}$	1.	Found. 2.	3.
C	28.30	28.20		
H	1.88	2.09		
Ca	18.87	18.77	18.97	18.78

In confirmation of these results it seemed advisable to isolate the methylurea which should be formed as the second product of the reaction. We therefore oxidized with hydrochloric acid and potassic chlorate, according to the method of Schlieper, evaporated at a gentle heat until the greater part of the excess of hydrochloric acid was driven off, and then separated from the potassic chloride with absolute alcohol. The residue left by the evaporation of the alcohol at a low temperature gave with nitric acid crystals of methylurea nitrate, which were purified by pressing between folds of paper and recrystallization from water.

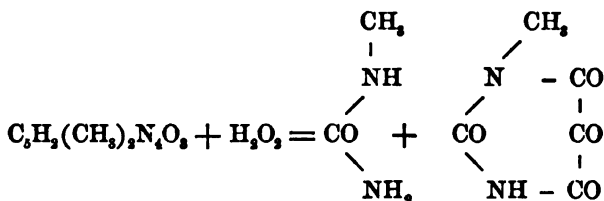
0.2464 gr. gave 0.1635 gr.  $\text{CO}_2$  and 0.1147 gr.  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_2\text{H}_7\text{N}_2\text{O}_4$	Found.
C	17.81	18.09
H	5.11	5.15

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\* These Proceedings, Vol. XII. p. 88.

This reaction may therefore be written:—



By the oxidation with potassic chlorate we have, however, invariably observed the formation of a small quantity of a crystalline substance, which we have as yet been unable to obtain in sufficient quantity for investigation. When the residue obtained by evaporation after oxidation was diluted with water, well-formed transparent prisms, pointed at either end, gradually separated, which could be recrystallized from hot water. The quantity formed was extremely small, and, although we modified the process in many ways, we have thus far been unable to increase the yield. At present, therefore, we can do no more than describe the few experiments we have been able to make with the small quantity at our disposal. The substance was readily soluble in hot water, sparingly soluble in cold water or in alcohol. In concentrated nitric acid it dissolved on warming, and crystallized out apparently unchanged on cooling. With ammonia it gave no red color. On heating it melted at about  $160^\circ$ . An analysis gave numbers which correspond more nearly with those required by  $\text{C}_6\text{H}_5\text{N}_4\text{O}_8$  than by any other simple formula.

0.2078 gr. gave 0.3259 gr.  $\text{CO}_2$  and 0.0788 gr.  $\text{H}_2\text{O}$ .

0.1459 gr. gave 25.6 cc. nitrogen at  $16^\circ$  and 720 mm. pressure.

	Calculated for $\text{C}_6\text{H}_5\text{N}_4\text{O}_8$	Found.
C	42.26	42.77
H	4.23	4.21
N	19.72	19.27

Although the substance possessed acid properties, we were unable to prepare its salts. On boiling with a solution of baric hydrate it was decomposed with the separation of baric carbonate. In the distillate the presence of ammonia and an amine, without doubt methylamine, could be proved by qualitative tests, and in the residue was an acid whose barium and lead salts were sparingly soluble in water, but which we were unable to identify on account of our very limited supply of material.



By the long-continued action of nitric acid upon dimethyluric acid methylparaban is formed. After boiling with nitric acid of sp. gr. 1.3 till a drop of the solution gave no coloration with ammonia, the solution was evaporated on the water-bath until the excess of acid was driven off and the sirupy residue diluted with a little water. The crystals which separated were pressed with paper and recrystallized from hot water.

Thus prepared the substance melted at  $149^{\circ}$ , sublimed slowly at  $100^{\circ}$ , readily at higher temperatures, and gave on analysis the percentages corresponding to methylparaban.

0.2838 gr. gave 0.3886 gr.  $\text{CO}_2$  and 0.0879 gr.  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_8\text{H}(\text{CH}_3)_2\text{N}_2\text{O}_6$	Found.
C	87.50	87.35
H	3.13	3.45

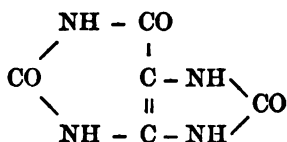
By the oxidation of dimethyluric acid with potassic permanganate in alkaline solution, we have been unable to prepare the corresponding dimethylallantoin. The acid either undergoes a more radical decomposition, or more probably the assimilation of water takes place more readily than in case of allantoin or even methylallantoin and the dimethylallantoic acid results.

We made several attempts to isolate from the uncrystallizable product of the oxidation various salts of the dimethylallantoic acid, but found them so uninviting in their character, that we could hardly hope to effect their purification.

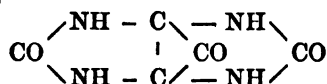
Since considerable time must of necessity elapse before further results can be obtained in this investigation, it may not be out of place to call attention to one inference concerning the structure of uric acid which may fairly be drawn from the facts thus far established.

It has been shown that the two hydrogen atoms of uric acid which are replaced in the formation of salts are directly connected with two different nitrogen atoms; furthermore, when methyl groups are introduced in the place of these hydrogen atoms, that two other hydrogen atoms may then be replaced by metals. The only simple explanation of this behavior would seem to be that the four hydrogen atoms of uric acid are attached to four different nitrogen atoms, and that only two of these hydrogen atoms can be replaced at the same time

by strongly basic radicals. Of the many structure-formulæ which have thus far been proposed for uric acid only two contain this arrangement of the hydrogen atoms. These are the formulæ of Medicus,\* —



and of Fittig,† —



Further discussion of these formulæ, or of others fulfilling the same conditions, must be reserved for a subsequent paper.

H. B. H.

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\* Ann. Chem. u. Pharm., clxxv. 243.

† Grundsiss. der Organischen Chemie, 10th edition, p. 300.

## XIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COM-  
POUNDS.

By C. LORING JACKSON.

EIGHTH PAPER.

SUBSTITUTED BENZALDEHYDES.

By J. FLEMING WHITE.

Presented April 14, 1880.

THE ortho- and parachlorbenzaldehydes are the only compounds of this class containing a single halogen atom which have been described heretofore. The former, made by Henry \* from salicylaldehyde by treating it with an excess of phosphoric pentachloride and decomposing the orthochlorbenzalchloride,  $C_6H_4ClCHCl_2$ , formed with water in a sealed tube at  $170^\circ$ , was a heavy colorless oil boiling between  $210^\circ$  and  $220^\circ$  and oxidized even by the air into orthochlorbenzoic acid.

The so-called parachlorbenzaldehyde was first made by Beilstein and Kuhlberg † by boiling chlorbenzylchloride,  $C_6H_4ClCH_2Cl$ , with plumbic nitrate and water, according to the method of Lauth and Grimaux; ‡ also by heating chlorbenzalchloride,  $C_6H_4ClCHCl_2$ , with water in a sealed tube at  $170^\circ$ , and by treating benzaldehyde with chlorine in presence of iodine. Later, Berlin § obtained it by distilling trichlorbenzylamine,  $(C_6H_4ClCH_2)_3N$ , with bromine and water, and Sintenis || by the action of chlorine on chlorbenzylethylether,  $C_6H_4ClCH_2OC_2H_5$ . They all describe it as a heavy oil, and Berlin gives its boiling-point as  $210^\circ$ – $220^\circ$ .

\* Ber. d. ch. G., 1869, p. 135.

§ Ann. Chem. Pharm., cli. 140.

† Ann. Chem. Pharm., cxlvii. 352.

|| Ber. d. ch. G., 1871, p. 697.

‡ Ibid., cxliii. 80.

As the chlorine compounds used by Beilstein and Kuhlberg, Berlin, and Sintenis were all made by the action of chlorine on toluol in the cold, and must therefore have contained the corresponding ortho-compounds,\* a revision of their work is necessary.

*Parachlorbenzaldehyde*,  $C_6H_4ClCOH$ , was made by boiling 10 gra. of parachlorbenzylbromide, melting-point  $48\frac{1}{2}^\circ$ , with 14 gra. of plumbic nitrate and 100 gra. of water for three days in a flask with a return-cooler, which was kept full of carbonic dioxide during the boiling and subsequent distillations to prevent oxidation of the aldehyde by the air. The aldehyde, separated by distillation from the plumbic bromide formed, solidified in the cooler in long white needles, which were purified by solution in acid sodic sulphite and filtering; the filtrate concentrated by evaporation deposited on cooling crystals of the double salt of the aldehyde and acid sulphite, which were washed twice with cold alcohol, dried, dissolved in a small quantity of hot water, and decomposed by distillation with solid sodic carbonate. The pure aldehyde, thus obtained, was dried over sulphuric acid in an atmosphere of carbonic dioxide and analyzed.

0.2112 gr. gave on combustion 0.4613 gr.  $CO_2$  and 0.0680 gr.  $H_2O$ .

	Calculated for $C_6H_4ClO$ .	Found.
Carbon	59.78	59.56
Hydrogen	3.56	3.57

*Properties.* Long white needles melting at  $47\frac{1}{2}^\circ$ , which sublime very easily; slightly soluble in water, very soluble in alcohol, ether, benzole, carbonic disulphide, and glacial acetic acid. Potassic permanganate oxidizes it rapidly, air slowly, converting it into parachlorbenzoic acid.

The following substituted aldehydes were prepared from the corresponding bromides by the same method. In solubility they all resemble the parachlorbenzaldehyde.

*Parabrombenzaldehyde*,  $C_6H_4BrCOH$ .

0.5000 gr. of the substance gave on combustion 0.8268 gr.  $CO_2$  and 0.1298 gr.  $H_2O$ .

	Calculated for $C_6H_4BrO$ .	Found.
Carbon	45.40	45.10
Hydrogen	2.70	2.88

Long white needles melting at  $57^\circ$ . With oxidizing agents or air it forms parabrombenzoic acid.

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\* These Proceedings, Vol. XIV. p. 54.

*Paraiodbenzaldehyde*,  $C_6H_4IOH$ .

0.7339 gr. of substance gave on combustion 0.9665 gr.  $CO_2$ . The hydrogen was unfortunately lost.

	Calculated for $C_6H_4IO$ .	Found.
Carbon	36.20	35.90

White needles melting at  $78^\circ$ . With oxidizing agents it forms paraiodbenzoic acid.

*Metabrombenzaldehyde*,  $C_6H_4BrCOH$ .

0.5900 gr. of substance gave on combustion 0.9800 gr.  $CO_2$  and 0.1320 gr.  $H_2O$ .

	Calculated for $C_6H_4BrO$ .	Found.
Carbon	45.40	45.30
Hydrogen	2.70	2.49

A colorless heavy oil, showing no signs of solidifying even in a freezing mixture of ice and salt. With oxidizing agents, or on exposure to the air, gives very easily metabrombenzoic acid.

*Orthobrombenzaldehyde*,  $C_6H_4BrCOH$ , was prepared from the liquid orthobrombenzylbromide, as this work was done before it had been obtained in the solid state. Instead of distilling the product of the reaction, the plumbic bromide and water were decanted while hot, leaving the aldehyde as a heavy oil, which was washed with water, purified as before described with acid sodic sulphite, dried, and analyzed.

0.5440 gr. of substance gave, on combustion, 0.8990 gr.  $CO_2$  and 0.1476 gr.  $H_2O$ .

	Calculated for $C_6H_4BrO$ .	Found.
Carbon	45.40	45.08
Hydrogen	2.70	3.01

A heavy colorless oil, much more rapidly oxidized by the air than any of the other substances described in this paper.

The three para-compounds yielded, when treated in alcoholic solution with sulphuretted hydrogen, the thioaldehyde, as a reddish white varnish, which it did not seem worth while to investigate.

## XIV.

## ON A MECHANICAL ATTACHMENT FOR EQUATORIAL MOUNTINGS, TO FACILITATE SWEEPING IN RIGHT ASCENSION.

BY D. P. TODD, M.A.

Presented May 12, 1880.

NOT infrequently it happens that the astronomer has occasion to search a portion of the heavens defined in right ascension and north polar distance. The general method of such searches consists in a subdivision of the entire area into a number of zones, — of a convenient length in right ascension and of a width in declination somewhat less than the field of view of the eye-piece. No special difficulty attaches to the mere shifting from one zone to another in declination: this may be done quite automatically by a known amount of rotation of a tangent-screw applied to the declination-circle; or the observer, watching some star that happens to be in the right part of the field, can turn the tangent-screw until the instrument points upon the new zone.

To define the limits of the several zones in right ascension, however, is not so simple a matter. If it is not important that the limits of the zones be accurately observed, and neighboring stars are readily visible, perhaps the observer may get along fairly well by simple eye-alignment. Or, if he has an assistant at the right-ascension-circle, he can be duly apprised of the termination of the zones. Or, each sweep in right ascension may be terminated quite at random, the telescope being moved so far each time that the entire zone shall be surely covered: there must, nevertheless, be frequent reference to the clock and circle.

All of these methods take a deal more time than is employed in the actual search at the eye-piece. If, without leaving the eye-piece, the observer had some convenient way of knowing the moment when his telescope had reached the end of the zone, much of his time would be

saved, and the search could be prosecuted with greater rapidity. In the autumn of 1877, I devised for this purpose the piece of mechanism which I am about to describe.

In sweeping over the zones in right ascension, the clock-motion and sector are, of course, detached from the polar axis. The arc of the sector is to be graduated, as the right-ascension-circle is graduated; it need be only a continuous graduation of hours and parts thereof. Sliding upon this graduation, or adjacent to it, are two metallic vernier-like pieces, both of which are furnished with screws for clamping to any part of the graduated sector-arc. Each of these verniers carries a projecting metallic point, attached to it on a line joining the centre of the polar axis and the zero point of the vernier. Revolving freely about the polar axis, and adjacent to the sector, is a collar, carrying a projecting arm the end of which will just touch the metallic points attached to the verniers. This collar has a screw for clamping it to the polar axis, just as the sector has. And, moreover, electric apparatus is so disposed that, whenever the end of the projecting arm comes in contact with either of the metallic points attached to the verniers, a telegraphic sounder shall beat, or an electric bell shall ring.

The apparatus is now complete. Its use is as follows : —

By means of the graduation on the sector, the two verniers contiguous to it are set at a distance apart equal to the length of the zones to be searched. The sector is then unclamped from the polar axis and connected with the clock, and the clock set a-going. The telescope is then set to the right ascension of one end of the zones to be searched, and the projecting arm is at the same time brought into contact with the metallic point of the corresponding vernier, and clamped to the polar axis in that position. After the declination-circle is set, the whole instrument is ready for the search, and it is not necessary to remove the eye from the telescope, as the click of the sounder or the ring of the bell apprises the ear of the observer whenever the telescope reaches either limit of the zone in right ascension.

I venture to predict the usefulness of this piece of apparatus in the search for intramercorial planets during total solar eclipses, when the available time is a minimum, and the area to be swept over is comparatively quite extended. I hope, also, for its successful application in orbit-sweeping; it was in connection with the execution of such a search that the apparatus was devised. Furthermore, in the event of search for an object so faint as to require a very large telescope, I

think the device will be found of especial utility ; as, in the case of cumbrous mountings, the ingenious modification of an equatorial into an orbit-sweeper, suggested by Sir George Airy, does not appear to be convenient in application. If the orbit is somewhat inclined to the equator, it will be found convenient to stop the equatorial clock for a few seconds after a given space in declination has been passed over. A new system of zones is then begun.

NAUTICAL ALMANAC OFFICE, WASHINGTON,  
May 8, 1880.



## XV.

ON THE PRESENT STATE OF THE QUESTION OF  
STANDARDS OF LENGTH.

BY W. A. ROGERS.

Presented April 14, 1880.

It is not my intention in this paper to enter into a minute account of the construction and comparison of the various standards of length which have been made the basis of measurements, either in trigonometrical surveys of the earth's surface, or in more strictly physical investigations. Many of these possess a certain historical interest, even when they have but little inherent value. For information of this kind, the reader is referred to the references at the end of this paper.

I shall confine myself to a consideration of those standards of length which are in actual use, and which have the authority and sanction of either national or international law.

Three natural units have been proposed as the basis of a standard of length, as follows:—

I. The length of a pendulum beating seconds in a vacuum at the level of the sea in the latitude of London.

II. One ten-millionth part of a quadrant of the earth's surface.

III. The length of a wave of light of given refrangibility.

It is generally supposed that the yard of Great Britain was founded upon the first of the natural units named, but it will be seen from the act of Parliament legalizing the standards prepared by the Royal Commission, signed June 17, 1824, that the reference of the standard of length to this unit refers to its restoration in case of loss or destruction, and not to its original construction. Notwithstanding many experiments were made at this time by Kater and others for the purpose of ascertaining the length of the standard expressed in terms of the length of a seconds pendulum, the yard actually legalized was con-

structed from Graham's scale by Bird, in 1760. It is marked, "Standard 1760."

The reason assigned for selecting Bird's "Standard 1760" was its close agreement with Shuckburgh's scale ( $0-36^{\text{in.}}$ ), made by Troughton in 1798, with which the pendulum and the meter had been compared, and of which a fac-simile was known to exist at Geneva. It is interesting to note, in passing, that, previous to Shuckburgh, all transfers were made by means of beam compasses, and all comparisons were made in the same way. The first use of optical means of comparison must be credited to Troughton in 1798, when he transferred Bird's scale for Shuckburgh. The following is the act legalizing the standards:—

"SECTION I. Be it enacted . . . that from and after the first day of May one thousand eight hundred and twenty-five, the Straight Line or Distance between the Centres of the Two Points in the Gold Studs in the Straight Brass Rod, now in the Custody of the Clerk of the House of Commons, whereon the Words and Figures 'Standard Yard 1760' are engraved, shall be and the same is hereby declared to be the original and genuine Standard of that Measure of Length or lineal Extension called a Yard; and that the same Straight Line or Distance between the Centres of the said Two Points in the said Gold Studs in the said Brass Rod, the Brass being at the temperature of Sixty-two Degrees by Fahrenheit's Thermometer, shall be and is hereby denominated the 'Imperial Standard Yard.' . . .

"SECTION III. And whereas it is expedient that the said Standard Yard, if lost, destroyed, defaced, or otherwise injured, should be restored to the same Length by reference to some invariable natural Standard; And whereas it has been ascertained by the Commissioners appointed by His Majesty to inquire into the subject of Weights and Measures, that the said Yard hereby declared to be the Imperial Standard Yard, when compared with a Pendulum vibrating Seconds of Mean Time in the Latitude of London in a Vacuum at the Level of the Sea is in the proportion of Thirty-Six Inches to Thirty-Nine Inches and one thousand three hundred and ninety-three ten-thousandth Parts of an Inch: Be it therefore enacted and declared, That if at any Time hereafter the said Imperial Standard Yard shall be lost or shall be in any Manner destroyed, defaced, or otherwise injured, it shall and may be restored by making a new Standard Yard, bearing the same Proportion to such Pendulum as aforesaid as the said Imperial Standard Yard bears to such Pendulum."

On the 16th of October, 1834, both houses of Parliament were con-

sumed by fire. The bar of 1760 was recovered, but in a condition which rendered it useless as a standard, one of the gold plugs having been melted out. It now became necessary to decide whether it should be restored in accordance with the act of June 17, 1824. Since the passage of the act, it had been shown that all the elements which were defined in the act for restoration were subject to some doubt. Dr. Young had shown that the reduction to the level of the sea was doubtful. Both Bessel and Baily had shown that the reduction for the weight of the air was erroneous. Baily had thrown doubt upon the estimated specific gravity of the pendulum employed, and upon the accuracy of the agate planes, while Kater himself showed that sensible errors had been introduced in comparing the pendulum with Shuckburgh's scale.

In view of these facts, all attempts to restore the lost standard in accordance with the act of June, 1824, were abandoned. Instead, it was decided to attempt the restoration of the lost standard from the various standards which had been previously compared with it. There were available for this purpose,—

Shuckburgh's scale ( $0-36^{\text{in}}$ );

Shuckburgh's scale, with Kater's authority;

The yard of the Royal Society, constructed by Kater;

The Royal Astronomical Society's brass tubular scale;

Two iron bars, marked  $A_1$  and  $A_2$ , belonging to the Ordnance Department, and preserved in the office of the Trigonometrical Survey.

The restoration of the standard was placed in the hands of Sir Francis Baily. At his death, in August, 1844, he had done little more than complete the provisional inquiries required before attempting the final construction. He had, however, after many experiments, decided upon the material of which the new standard should be composed. It has since his time been known as Baily's metal. Its composition is, copper 16, tin  $2\frac{1}{2}$ , zinc 1.

Upon the death of Mr. Baily, the work of restoration was committed to the Rev. R. Sheepshanks. Sir George Airy, in his account of the construction of the new national standards of length, has given an exceedingly interesting communication from Mr. Sheepshanks (*Philosophical Transactions*, 1857, p. 661), detailing the means he employed for the restoration of the lost standard. He first constructed a brass bar, as a working standard. This "brass bar 2" was compared with all the standards which Mr. Sheepshanks considered properly available for this purpose, with the following results:—

Inches.

Brass bar 2 = 36.000280 by Shuckburgh [10 - 46<sup>in</sup>].  
 = 36.000084 by Shuckburgh [0 - 36<sup>in</sup>, Kater].  
 = 36.000229 by Kater's scale.  
 = 36.000303 by A<sub>1</sub> compared in 1834.  
 = 36.000275 by A<sub>2</sub> compared in 1834.

Mean, 36.000234

He assumed : —

Brass bar 2 = 36.00025 inches of the lost imperial standard at 62° Fahrenheit.

It is stated both in Appletons' and in Johnson's Encyclopædias that the yard of the Astronomical Society is the principal authority upon which the new standard rests. It will be seen from the above that this statement is erroneous.

The Imperial Standard Yard, known as "Bronze 19," or, according to the new nomenclature, as No. 1, was constructed according to this equation. It is made of Baily's metal, and has the following dimensions, viz. : —

Length = 38 inches.  
 Width = 1 inch.  
 Depth = 1 inch.

Gold plugs are inserted in wells sunk one half of the depth of the bar. The graduations are on these gold plugs.

Through the kindness of Mr. Chaney, the Warden of the Standards, I have recently had the pleasure of assisting him in comparing my own working standard yard with this bar. I have never seen lines better adapted to exact measurements. They have remarkably smooth edges, and are about one three-thousandth of an inch in width. Even for the most rigid scientific investigations, they are in every respect of unrivalled excellence.

Bronze No. 1 is the national standard, and is kept in what is known as the "Strong Room" of Old Palace Yard. Besides this bar, four Parliamentary copies were made, of which one copy is kept at the Royal Mint, one is in charge of the Royal Society, one is immured in the new Westminster Palace, and the other is kept at the Royal Observatory, Greenwich. Forty copies were prepared on Baily's metal. Of these only two are exactly standard at 62°, viz. Bronze 19, and Bronze 28, which is kept at the Royal Observatory as an accessible representation of the national standard. All the other copies have an equation with respect to No. 1; but instead of giving this equation,

the degree at which each bar is standard is given. These bars have all been distributed among different governments.

The standards prepared by Mr. Sheepshanks were legalized by act of Parliament passed July 30, 1855.

Two platinum bars — one a line-measure and the other an end-measure — form the basis of the metric standard of length at present in use in Great Britain. These bars have the following dimensions : —

	Line-Meter.	End-Meter.
Length,	41.0 inches.	39.37 inches.
Breadth,	1.0	1.00
Thickness,	0.211	0.287

The line-meter has the words "Royal Society, 45," engraved on the under side. The defining lines run nearly across the face of the bar, and there is no cross line to indicate the exact points from which measures are to be made. Arrows, arbitrarily placed, now indicate the points from which all the later measures have been made. The lines on this bar have become so obliterated that it is found impossible to see them with the method of illumination formerly in use. At the request of Mr. Chaney, I employed Mr. Crouch, of London, to construct two new objectives for the microscopes of the comparator, to which were adapted two of Tolles's interior illuminators for viewing opaque objects. The magnifying power was increased between five and six times, and the illumination was so much improved that there was no difficulty whatever in seeing the lines of this bar.

The end-meter has the words "Mètre à Bouts" engraved on one side, and the words "Fortin à Paris, Royal Society 44," on the other side. At the present time, this standard is not in a condition to admit of accurate measurements. The edges of the end surfaces are indented, and there is a raised burr on one end. These bars, together with the original bars compared by Hassler in 1832, are the only recognized standards which have ever been compared with the Meter of the Archives. They form, therefore, the real basis of our present knowledge of the relative length of the meter and of the yard. I shall presently recur to this important matter.

The line-meter was transferred by Troughton and Simms to a bar of Baily's metal in 1869. Kater's reduction to the Meter of the Archives was applied in the transfer. The Imperial Yard was also transferred to the same bar. The lines are drawn upon gold plugs, which are not, however, inserted in wells. At the distance of 39.37 inches from the first plug the "meter plug" is inserted. This meter is

the one from which Chisholm obtained his value of the equation between the meter and the yard. It is now the working standard meter of the Exchequer.

A second natural unit, viz. one ten-millionth part of a quadrant of the earth's surface, was adopted at the close of the last century as the basis of the metric system. In March, 1791, a committee of the Institute of France, consisting of fifteen members, including Borda, Lagrange, Laplace, Mongé, and Condorcet, recommended this unit as a standard of linear measure. It is interesting to note that the Commission was largely international in its composition. Besides the members of the Institute, there were delegates from the Republic of the Netherlands, from Sardinia, Denmark, Spain, Tuscany, the Roman Republic, the Cisalpine Republic, the Ligurian Republic, the Swiss Confederation, and from Piedmont. Their report was sanctioned by the Assembly, and an arc of the meridian passing through Paris, and extending from Dunkirk to Barcelona (stations differing about  $10^{\circ}$  in latitude), was measured with great care by Méchain and Delambre. By combining the results of this survey with arcs previously measured in Peru and Sweden, the length of a meridional quadrant passing through Paris was ascertained. For the measurement of base lines, two separate toise end-measures were employed, each assumed to be equivalent to the toise of Peru. From these standards, four iron bars were prepared, having their ends carefully ground and polished until they were exactly comparable with each other, and until each had the required length. One of these original bars, bearing upon it the stamp of the Commission, is now in the possession of the United States Coast Survey. It is understood to be the only copy now in existence. One bar was chosen as the standard of France, and from it was constructed the platinum "*Mètre des Archives*." Two similar meters, made at the same time and in the same manner, are now in existence, viz. the "*Mètre du Conservatoire*," and the "*Mètre de l'Observatoire*." All of these meters are end-measures, and have about the same dimensions as the English platinum meters already described. The equation between the "*Mètre des Archives*" and the "*Mètre du Conservatoire*" is small. That between the "*Mètre des Archives*" and the "*Mètre de l'Observatoire*" is not well determined. Only one line-measure is known to have been made at the time of the construction of the end-measures. This was transferred from the "*Mètre de l'Observatoire*," probably about two years after the adoption of the "*Mètre des Archives*" as a standard.

In 1870, a commission was formed at Paris, under the title "Com-

mission International du Mètre," for the purpose of settling all doubts in regard to the value and permanence of the unit bases. In 1874, this commission decided to maintain at Paris an "International Bureau of Weights and Measures, to be supported by *pro rata* contributions from all the signing powers, and charged with the care of the prototype standards, and with the duty of constructing and verifying copies of those standards, not only for the powers interested, but for other governments, for corporations, and even for private individuals who should apply for them, and who should be willing to pay the expense attending their construction and comparison."

It is not necessary to record here the considerations which led the Commission to abandon all attempts to establish a standard which should conform to the natural unit, in accordance with which the original meters were constructed. It is sufficient to say that the Commission decided that the "Mètre des Archives" shall be recognized and perpetuated forever as the true base of the measure of extension, without regard to the doubtful questions which have been raised concerning its correspondence with its theoretical value. The first resolution of the "Convention du Mètre," signed May 20, 1875, reads as follows: "For the execution of the international meter, the Mètre des Archives, in the state in which it is found, is taken as the point of departure."

The Convention adopted twenty-one resolutions respecting the meter, of which the most important are the following: —

"IV. Though deciding that the new international meter shall be a line-meter, of which every country shall receive identical copies, constructed at the same time as the line prototype, the Commission will nevertheless undertake to construct a certain number of end-measure standards for the countries which shall express a desire for them, and the equations of these end-meters with respect to the new line prototype shall be determined with equal care by the International Commission.

"V. The international meter shall be of the length of the meter at 0° C.

"VI. In the fabrication of the meters, an alloy shall be employed, composed of 90 parts of platinum and 10 parts of iridium, with an allowance of two per cent variation, more or less."

"IX. The bars of platinum-iridium, upon which the lines are to be traced, shall be 102 centimeters in length, and their transverse section shall be represented by a model described in a note by M. Tresca."

"XIII. The method of M. Fizeau shall be employed in determin-

ing the expansion of the platinum-iridium, of which the meters are formed.

"XIV. The prototype shall be submitted to the best possible process for the determination of the absolute coefficient of expansion of the whole meters. These measures shall be made separately, at least at five different temperatures comprised between  $0^{\circ}$  and  $40^{\circ}$  C."

"XVII. The comparisons shall be made by immersing the new standards in a liquid and in air, but with the reservation that the standard of the Archives shall not be immersed in any liquid until the close of the operations.

"XVIII. The tracing of the line-meters, and their first comparison with the 'Mètre des Archives,' shall be effected by the process of M. Fizeau."

In order to gain a clear understanding of what has been accomplished in accordance with these resolutions, it is necessary to distinguish between the operations of the French section of the Commission and those of the International Bureau. The construction of the prototypes from the "Mètre des Archives" was naturally committed to the French section, the primary standard being the property of the French government, the responsible authority for its preservation in a state of perfect integrity.

The prototypes thus prepared, after delivery to the International Commission, and after their formal acceptance by the Commission, are to be subjected to the various tests provided for by the articles of the convention. Finally, either one of these prototypes, or, perhaps, the mean of two or three of them, will be officially declared to be the true and final base of reference in all measurements of linear extension.

The International Bureau is now prepared for its share of the work. The buildings are completed, the instruments of comparison are in position, and nearly all of the provisional investigations required have been completed. The present delay must be charged to the unfortunate dead-lock between the Commission and the French section, the Commission refusing to accept the prototypes prepared by M. Tresca, mainly on the ground that the material of which the standards are made is not, in its present condition, a pure alloy of platinum and iridium, but that it contains, as is asserted, nearly two per cent of iron.

The International Bureau at the present time has no standards which have been compared directly with the "Mètre des Archives." It has three provisional meters, all of which have been indirectly compared with the primary standard. It has a meter made by Repsold, one made by Hermann and Pfister, of Berne, Switzerland, and one



made by Brunner Frères, of Paris, which is presumably a copy of the line-meter derived from the meter of the Observatory. The meter by Brunner Frères, the tracings on which are very good, is taken as the present provisional standard.

The buildings of the International Bureau are situated on the summit of a high hill at Breteuil, on the direct road from Paris to Versailles. The location is an admirable one in every point of view. During my recent visit to Paris, a very kind letter of introduction from Professor St. Claire Deville to Dr. Pernet, the Director of the Bureau, led to a very interesting visit to this establishment. There are three principal observing-rooms, perhaps eighty meters square. The walls are composed of corrugated metal, the waves running longitudinally. The rooms are lighted by a circular skylight only.

In one room is found the apparatus for comparing standards of weight, under the charge of Dr. Marek. There is here a marvelously perfect apparatus for weighing in a vacuum, made by Bunge, of Hamburg. The observer is enabled to perform every part of the operation of weighing, stationed at a distance of six or eight meters. There is also a fine balance by Rupprecht, of Vienna.

In a second room, the instruments for determining the coefficients of expansion are mounted. This department is under the charge of Dr. Benoit. Both the method by immersion in a liquid, and the method of M. Fizeau, are employed. The latter method is described in the *Comptes Rendus* for 1866. It is also described in the Proceedings of the Royal Society of Nov. 30, 1866. I quote from the Proceedings: "In M. Fizeau's observations, he has availed himself of the possibility of forming Newton's rings with the monochromatic sodium light, when one of the interfering rays is 52.205 waves in advance of the other, a fact which, conjointly with M. Foucault, he announced in 1849. Using the length of a wave of sodium light 0.0005888 mm. [0.00002318<sup>in</sup>.] as a standard of measure, the position of a ring being observable to within  $\frac{1}{10}$  of the distance between two consecutive rings, the *variation* of the distances between the two surfaces producing Newton's rings can be measured within 0.00002944 mm. or 0.0001159<sup>in</sup>." The results by this method, and those obtained by immersion in a liquid, are found to show a good agreement. The chief objection to its use is found in the fact that the method is only applicable to pieces of metal not much exceeding one centimeter in length. It must be assumed that the whole bar has the same coefficient as the small portion of it upon which the observation rests. In the discussion of the coefficient of the Mètre des Archives, it will be interesting to compare the value finally derived with the value

found by M. Fizeau from a small section of the original bar which has been preserved in the Archives.

A third room of the building is devoted to the comparison of standards. This department is under the charge of Dr. Pernet. Here is mounted a fine comparator by Brunner Frères, built at a cost of 15,000 francs. A universal comparator by Starke, of Vienna, and costing 28,000 francs, will soon be in position. This apparatus will allow comparisons between standards two meters in length. There are also attachments for comparing subdivisions.

The Bureau has also a very perfect apparatus for determining the zero point and the boiling point of the thermometers employed in the comparisons. The *minimum* point of freezing is first found. To this minimum reading are applied the *variations* of the zero point, which are investigated for each thermometer. The thermometers are made by Baudin, of Paris. He makes two kinds. In one, the tubes are divided into a scale of equal parts; in the other, all the errors, except those of the zero and boiling points, are included in the graduations. The thermometers are read to single hundredths of a degree. It is the experience of Dr. Pernet that all the standard thermometers of Baudin will agree *inter se* within three hundredths of a degree.

I now pass to a consideration of the operations of the French Section, which are conducted in the building of the "École des Arts et Metiers," usually called the Conservatory.

Through the kindness of M. Tresca, who is the secretary of the Section, and, since the death of General Morin, the acting Director of the Conservatory, I was able, during a recent visit to Paris, to make a careful study of the entire operation of converting the "Mètre des Archives" into an equivalent line-meter. Notwithstanding the pressure of the official duties of M. Tresca, which were at the time of my visit especially great, owing to the illness and death of General Morin, the Director of the Conservatory, he gave me several hours each day, explaining in detail each step of the operation, from the melting of the platinum-iridium to the final comparison of the completed bar with the "Mètre des Archives." As the result of this somewhat critical study, I express the unqualified opinion that M. Tresca is entirely master of the problem. His methods and his results are at least beyond present criticism. In this I do not, however, include the method adopted of comparing end-measures with line-measures. This method, which is sometimes credited to Fizeau, and sometimes to Wild, seems to me to be radically defective.

To the end of a plate having the same thickness as the "Mètre

des Archives," a strip of very thin platinum, terminating in a sharp point, is attached. The reflection of this point from the end of the bar gives the means of observing the point of contact without actually touching the surface. This method seems to be a necessity in this case, since a statute law forbids contact of any kind whatever. If it was not for this necessary limitation, a much better method could be employed. Still, it is the opinion of M. Tresca that the absolute error of the line prototype can be reduced below  $1\ \mu = .001\ \text{mm}$ .

On account of the difficulties attending the transfer from an end-measure to a line-measure, M. Tresca has adopted the plan of transferring one line-meter with the utmost precision. This copy, which he calls his "working meter," has occupied his attention for several months. He is confident that every source of error has been eliminated. This line-meter will be the basis of the final standard, since the Commission will accept without question the definitive transfer offered by the French Section after the difficulties with respect to the question of material are removed. On this point there is no dispute. The real issue is this. The International Bureau ask of the French Section one or more bars of pure platinum, and several of platinum-iridium, with the definitive comparison with the "Mètre des Archives." The Commission contends that the bars already offered contain two per cent of iron, transferred through the process of drawing through dies. It contends also, that, by the process of drawing through dies, the bars remain in a state of strain. M. Tresca, on the other hand, contends that it is impossible that these criticisms can hold.

He admits that iron is transferred during the passage of the bars through the rollers, but this iron is extracted after each of the two hundred passages through the dies. M. Tresca also admits that the bars would be in a state of strain if left in the state in which they come through the dies, but he anneals them finally. As a proof of the correctness of this view, he gets exactly the same coefficient of expansion after each melting and casting of a given bar. Some bars have been melted and recast as many as ten times.

I heard but little said on the question of the alloy. The standard weights of the Bureau are made of platinum-iridium, and there seems to be no question about them.

The comparing rooms of the Conservatory are built as follows. First (a), there are the thick stone walls of the building; then (b), space filled with hay; (c), wooden walls; (d), space filled with cotton; (e), wooden walls, covered on the inside with paper. A copper room,

entirely enclosing the comparators, is built in the central part of the enclosed space. The microscopes of the comparators are 90 centimeters in length. Only the micrometer screws project through the upper wall of the copper room, so that the heat of the body of the observer can produce but a very slight effect. The value of one division of the micrometer is  $0.301 \mu$ .

There are two rooms of the same form and dimensions. One contains the longitudinal comparator, on which the transfers are made, and on which a series of comparisons is also made directly after the transfers, the two bars remaining in the same relative positions. The other room contains the transverse comparator, with which the final and definitive comparisons are made. These comparators were built by M. Froment.

The transfers and comparisons are only made after the bars have been in position, and subject to the same temperature, for a period of forty-eight hours. All the transfers and comparisons are made in air. The tracings are made between one and two o'clock in the morning. Even then, the jar of passing vehicles is very perceptible. The disturbance is, however, strictly local. No matter how great the tremors, no permanent movement of the bars can be seen.

In the *exposé* of the condition of the labors of the French Section to Sept. 22, 1879, will be found a complete statement of the present state of this great work.

A third natural unit of length has been proposed in the length of a wave of light of given refrangibility. It is extremely doubtful, however, whether this unit will ever come into extensive use. In the present state of the measurements of wave-lengths, the total number in a meter is known with a far less degree of exactness than can be assigned to the comparison of different meters. Probably the wave-length of the line D is as well known as that of any other line of the spectrum, and yet the measures by different investigators show large discordances. The meter as determined by different observers shows the following errors when compared with the value given by Angström:—

Authority.	Error.
Fraunhofer	— 1.1 mm.
Ditscheiner	+ 0.8
Angström	+ 0.0
Van der Willigen	— 0.3
Mascart	— 1.0
Bernard	— 1.0

In the wave-length equation  $\lambda = \epsilon \sin \theta$ ;  $\epsilon$  represents the *mean* distance between the lines of the grating. A certain number of isolated errors may occur in the ruling, which may entirely escape detection under the spectroscope. For example, one of the provisional gratings, ruled with the machine built for the writer at the Waltham Watch Factory, has errors of spacing which are easily measurable, and yet the grating will show 7 and possibly 10 lines between  $b_1$  and  $b_2$ , notwithstanding the fact that it is ruled upon commercial plate glass without finish.

Angström, in his investigations, found the distance between the extreme lines of the different gratings employed in terms of the Meter of the Archives; and the value of  $\epsilon$  was found by dividing the entire distance by the number of spaces. I cannot find that he made any investigation, either of the accidental or the systematic errors of the gratings. I am aware that it is commonly asserted that it is impossible for systematic errors of appreciable magnitude to exist in a grating which shows the solar lines sharply defined; but there are many evidences that not only isolated accidental errors, but periodic errors of a small but measurable magnitude, are not incompatible with apparently perfect definition. Since the periodic error of a screw may undergo considerable variations in value through a change of temperature, especially if this change is abrupt and violent, it does not seem possible to overcome them entirely, except by a rigid investigation immediately preceding the ruling of a given grating, and by the application of the corrections derived, during the process of ruling. It is without doubt true that the *mean* interval between the ruled lines can be expressed with a far greater degree of accuracy than any given space can be measured under the microscope; but I believe it to be possible to measure the errors of lines widely separated when there is no evidence of their existence in the appearance of the solar lines. Even the best gratings which have thus far been produced show traces of systematic error when they are examined with monochromatic light.

Briefly, then, whenever the yard with its subdivisions is adopted as the measure of length, the unit to which all measures must be referred is the Bronze bar deposited in the "Strong Room" of Old Palace Yard, London, known as the "Imperial Yard No. 1." It has been shown that all attempts to express the length of the Imperial Yard in terms of a natural unit have been abandoned.

Wherever the metric system has been adopted, either by legal enactment or by actual use in the absence of definite legislation, the plati-

num end-measure meter, deposited in the Archives of Paris, is the only ultimate standard of reference. Since sixteen governments have entered into the Convention, which, through the International Commission, has decided that this particular bar at 0° Centigrade shall be the unit to which all measures of extension shall be referred, there is hardly a possibility that a different unit will ever be adopted. Great Britain is the only prominent government that has declined to enter the Convention. The two platinum meters which have hitherto been the standard of reference in that country are, however, no longer adapted to the purposes of exact measurement. Besides, even here the ultimate reference is the Meter of the Archives, through the equation determined by Kater and Arago in 1818.

The only exception to the entire abandonment of all attempts to refer the meter to a natural unit is the indirect determination by Clarke and others of the length of this unit expressed in the ten-millionth part of a quadrant of the earth's surface. With the highest possible respect for the work which has been done by Colonel Clarke, it does not seem likely that his value of this unit will ever become generally adopted. In the first place, his arc of the meridian does not follow the definition upon which the Meter of the Archives was founded. In the reference to any given unit, the standard of length determined must be ascertained with a greater degree of exactness than that attainable in the comparison of different copies of this standard. It is the experience of the writer that the error involved in the comparison of different meters need not exceed one millionth of a meter. It is not probable that an arc of a meridian of the earth's surface extending over 90° of latitude can be measured with sufficient exactness to warrant the assignment of this degree of accuracy to the aliquot part of this distance, which we call a meter.

In the United States, the particular yard which, previous to 1856, was taken as a standard, is the distance between the 27th and the 63d inch of a scale by Troughton. It has never had other than an indirect legal authority. It was never legalized by act of Congress. It was, however, adopted by the Treasury Department. The first standards distributed to the States by the authority and direction of Congress were copies of this particular bar.

In 1856, "Bronze bar No. 11" was presented by the British Board of Trade to the United States. It is standard at 61°.79 Fahrenheit. Since this date, all measures of length which are expressed in terms of the yard have been referred to this particular unit. This change, by whatever authority it was made, was one clearly demanded in the inter-

est of science, and by the legalization of Bronze No. 1 as the Imperial Standard Yard, with which it had been most carefully compared; but I am not aware that it has ever been sanctioned by act of Congress.

For the metric system, the iron meter mentioned above has always been taken as the standard of reference. It has, however, no legal sanction. Neither in the case of the yard nor of the meter are comparisons usually made directly with the original standards.

The Saxton comparator consists of a brass bed-plate having V-shaped ways running the entire length. A slide carrying a microscope slides freely over these ways. A series of brass posts form a part of this bed, through which pass steel screws having conical ends, which have been tempered and polished. There are stops for the yard and for its subdivision into feet, and of one foot into inches. There are also stops for the meter and for its subdivision into decimeters, and of one decimeter into centimeters. By a very ingenious arrangement, the arm attached to the moving microscope plate can be brought into contact with any stop without loss of motion. The end stops for the yard and for the meter were many years ago set to correspond with "Bronze No. 11" at 58° nearly for the yard, and with the iron meter at 68° nearly. It is understood that the position of these stops with respect to the brass bed have never been changed. The standards which have been distributed since 1856 have been transferred from these distances at the temperatures at which they are standard. The yard in actual use at the Bureau of Weights and Measures, therefore, may be defined to be the distance between two steel stops attached to the bed of the Saxton comparator which corresponds to the length of "Bronze No. 11" at 58° nearly, and the meter may be defined to be the distance between two steel stops of the Saxton comparator which corresponds to the length of the iron meter corrected for the difference between its length at 32° and at 68° nearly. Recent comparisons indicate that these temperatures should be diminished, by a trifling amount, for the present distances between the stops, both for the yard and for the meter.

In May, 1878, by the kindness of Prof. J. E. Hilgard, Assistant in Charge of the United States Coast Survey, I was able to secure copies of both the yard and the meter, together with their subdivisions. On May 14, Dr. Clarke, who has charge of the standards, transferred the yard to a glass bar which I had previously prepared, and on the morning of May 17 the meter with its subdivisions was transferred to the same bar.

Upon my return to Cambridge, the relative relations between the

subdivisions were investigated, with the following results. A positive sign indicates that the measured space is too short; a negative sign, that it is too long.

*Subdivisions of the Yard.*

Feet.		Inches.		Inches.	
No.	Corrections.	No.	Corrections.	No.	Corrections.
1	+ .00069 in.	1.	+ .00075 in.	7	— .00037 in.
2	— .00022	2.	— .00004	8	+ .00062
3	— .00047	3.	— .00031	9	+ .00009
		4.	+ .00024	10	— .00097
		5.	+ .00064	11	— .00020
		6.	— .00011	12	— .00036

*Subdivisions of the Meter.*

Decimeters.		Centimeters.	
No.	Corrections.	No.	Corrections.
1	— .00080 cm.	1	— .00132 cm.
2	— .00018	2	+ .00021
3	— .00211	3	+ .00006
4	+ .00088	4	+ .00070
5	+ .00105	5	— .00070
6	+ .00142	6	+ .00003
7	+ .00041	7	+ .00100
8	— .00168	8	— .00019
9	— .00194	9	+ .00039
10	+ .00288	10	— .00016

These corrections involve the errors of transfer. No attempt was made to determine and apply the corrections due to the curvature of the ways upon which the slide carrying the microscope moves.

The subdivisions of the centimeter rest upon the authority of a centimeter subdivided into 100 equal parts by Brunner Frères, of Paris, for the office of the Coast Survey. By the permission of Professor Hilgard, I have made an extended series of comparisons between this unit and a centimeter derived from the screw of my own dividing engine. The comparisons were made by means of the comparator for short lengths, described in the American Microscopical Quarterly for April, 1879. The Brunner scale is divided on silver inlaid in brass. In my own scale, the graduations are upon glass.



Date.	Brunner.	Thermometer.	Rogers.	B. — R.
	No. div. of compar- ator in 1 cm.	°	No. div. of compar- ator in 1 cm.	No. div.
1878, May 14	3149.02	70.4	3148.80	+ 0.22
15	3149.95	74.8	3150.11	— 0.16
• 16	3149.33	63.0	3149.53	— 0.20
16	3149.51	63.8	3149.53	— 0.02
16	3149.63	64.0	3149.21	+ 0.42
17	3149.66	72.1	3149.20	+ 0.46
17 \	3149.66	72.1	3149.40	+ 0.26
18	3149.18	62.0	3149.44	— 0.26
18	3149.58	68.3	3149.37	+ 0.21
18	3149.57	68.8	3149.37	+ 0.20
18	3149.42	70.0	3149.12	+ 0.30
19	3149.52	69.8	3149.17	+ 0.35
20	3149.30	71.3	3149.01	+ 0.29
21	3149.55	71.1	3149.09	+ 0.46
Means,	3149.49	68.7	3149.31	+ 0.18

In terms of the Brunner scale, therefore, my own unit is .000317 cm.  
 $\times 0.18 = .000057$  cm. too short. Subsequent investigations have shown that both units contain errors of considerable magnitude when compared with the hundredth part of the Coast Survey meter at 68°.

The following are the relative errors of each millimeter expressed in terms of the entire length of the centimeter:—

Mm. No. 1	Brunner.	Rogers.
	Correction.	Correction.
1	+ .000082 cm.	— .000016 cm.
2	— .000091	+ .000025
3	— .000079	+ .000012
4	— .000070	+ .000016
5	+ .000038	+ .000029
6	+ .000002	— .000016
7	+ .000056	— .000044
8	+ .000035	— .000022
9	— .000080	— .000006
10	+ .000105	+ .000013

Notwithstanding the fact that great advances have been made in the science of exact measurements since the construction of the normal standards now in use, there are several problems connected with this subject which require further investigation. It is a well-known fact,

that, while the different results obtained in comparing two standards by one observer and with a given instrument usually indicate marvelous precision in the comparisons, a different observer with a different instrument will probably get results equally accordant *inter se*, but which nevertheless do not agree with those obtained by the first observer. Until all the sources of error involved in comparisons are investigated and eliminated, it will be useless to expect an agreement between different observers. Among the points which demand investigation, the following require special attention.

(a.) *The magnifying power of the microscopes employed, which is the best adapted to secure the greatest absolute accuracy in measurements.*

In all the earlier comparisons, microscopes of very low power were employed, varying from forty to sixty diameters. The International Commission, relying largely upon the recent investigations of Förster, have decided upon the low power of from forty to fifty diameters. M. Tresca, of the French section, on the contrary, is a firm believer in high powers; he prefers a power of about 400. The writer has had considerable experience on this subject, and always with results favorable to high powers. With a proper illumination, and with lines having smooth edges, a magnifying power of 900 can be used with great ease, even in the comparison of two meters upon a longitudinal comparator.

New microscopes have been recently attached to the microscopes of the meridian-circle of Harvard College Observatory. In order to be able to read the divisions of the circle, it was necessary to have one eye-piece with the same power as that furnished by the maker. A second eye-piece, giving nearly double the magnifying power, was attached to a swinging arm in such a manner that either eye-piece can be used at will. A sufficiently extended series of observations has now been made to justify the conclusion that the high-power eye-piece gives the most accurate results. Again, in the investigation of the errors of one of the circles of the instrument, a metal plate, having a graduated arc of  $15^\circ$ , is attached to the opposite circle under a one-inch objective, to which is attached the interior illuminator for viewing opaque objects, invented by Mr. R. B. Tolles, of Boston, in 1867, and also invented independently by M. Tresca, in 1871. The lines under this objective are sharply defined. The value of one division of the micrometer is only  $0''.12$  against  $1''.0$  for the regular microscopes. It is the experience of the writer, that it is quite as easy to make every reading fall within one division in one case as in the other. With

the ordinary form of illumination, however, the advantage of a high power would not be so apparent.

The value of one division of the micrometer depends both on the magnifying power of the microscope and on the pitch of the micrometer-screw. Those who advocate a low magnifying power usually prefer a screw having a small pitch. Further observations are needed to determine the best relation between the pitch of the screw and the magnifying power of the objective. The following are the values of one revolution of a few of the micrometer-screws which have been used in the comparison of standards:—

Observer.	Value of 1 division. Inch.	Observer.	Value of 1 division. Inch.
Troughton, 1798,	.0001000	Chaney, 1880, new objectives,	.0000058
Kater, 1818,	.0000428	Rogers, 1880, Comparator,—	
Hassler, 1832,	.0001000	Microscope A. { With 1 in. objective,	.0000197
Baily, 1832,	.0000500	Microscope B. { With $\frac{1}{2}$ in. objective,	.0000087
Baily, 1844,	.0000258	Microscope C. { With $\frac{1}{4}$ in. objective,	.0000047
Bache, 1856, May,	.0000383	Microscope D. { With $\frac{1}{2}$ in. and amplifier,	.0000028
Bache, 1856, October,	.0001000	Microscope E. { With 1 in. objective,	.0000079
Hilgard, Saxton Comparator,	.0001000	Microscope F. { With $\frac{1}{2}$ in. objective,	.0000085
Clarke, 1866,	.0000286	Microscope G. { With $\frac{1}{4}$ in. objective,	.0000019
Chaney, 1880, old objectives,	.0000319	Microscope H. { With $\frac{1}{4}$ in. and amplifier,	.0000011
Tresca, 1880, $0.301 \mu =$	.0000118	Internat. Comm., $1.0 \mu =$	.0000894

The writer is inclined to the opinion that one can measure with *certainty* only what one can see.

(b.) *The best method of illumination for opaque objects.*

I cannot better illustrate the necessity for a proper illumination in making exact measurements, than by saying that I have been obliged to reject a series of observations extending over a period of four months, for the simple reason that I finally discovered that during all this time I have never once seen the actual lines ruled, but only their image. I used a parabolic reflector, giving a beautiful *white* line on a black background. The lines were traced upon a steel surface nickel-plated, their width being about one ten-thousandth of an inch. Investigation showed that the positions of the lines could be changed by an amount more than half their width, by shifting the position of the parabolic reflector.

The method of illumination employed by Baily and Sheepshanks seems to me radically defective. With the microscopes used by Sheepshanks I found myself unable to separate lines ruled on a polished steel plate, though separated by an interval of only one-thousandth of a centimeter. As already stated, I have used with great satisfaction the

form of illumination described by Mr. Tolles in the Annual of Scientific Discovery for 1866-67. I found this form of illumination in use by M. Tresca since 1871. It has also been since described as an original invention by Professor Wild. Troughton and Simms also constructed microscopes with the same method of illumination as early as 1869, at the instance of Mr. Warner, a retired gentleman residing at Sussex Place, Brighton. According to the present evidence, the priority of publication must be assigned to Mr. Tolles. M. Tresca was without doubt the first to make an actual application of the method to exact measurements. The reader who is interested in pursuing this subject farther will find a full description of the method in the number of the Journal of the Royal Microscopical Society for August of the current year. It is sufficient to say here, that, as none of the light is lost by the reflection, it is easy to get all, and even more, than is needed. Diffused daylight falling upon the plane face of the prism inserted between the two front lenses affords an abundance of light for the most delicate tracings. With a one-inch objective of the form recently constructed by Mr. Tolles, lines 30,000 to the inch, ruled on a polished steel surface, are resolved with the greatest ease.

(c.) *The method of support which is best adapted to neutralize the effect of the flexure of the bars upon which the graduations are traced.*

In all the early measurements the standards were placed upon a planed surface of wood. Troughton, in comparing Shuckburgh's scale, fastened it to a bed of mahogany by means of three screws. Kater was the first to discover the variations due to the flexure of the bars on which the graduations were traced. He was also the first to suggest a neutral plane, in which the effect of flexure upon the length would be zero. At first he located this neutral plane in the middle of the bar, but from subsequent investigations he concluded that it was not quite one third of the thickness of the bar below the graduated surface. He reached the following conclusions\* :—

(1.) "That in a standard of lineal measure, traced upon the surface of a bar, an error arises from the thickness of the bar when it is placed upon a table, the surface of which is not plane."

(2.) "That this error in bars of the same material and of unequal thickness is within certain limits as the thickness of the bar, and depends upon the extension of that surface of the bar which becomes convex, and the compression of the surface which is concave."

(3.) "That the error to which the scale is liable from this cause is

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\* Phil. Trans., 1830.

directly as the versed sine of the curvature of the surface upon which the scale is placed."

(4.) "That this error very far exceeds that which would arise from the difference of length between the arc and its chord, under similar circumstances; so much so, that the sum of the errors from this cause in a bar one inch thick, with a versed sine of not one-hundredth of an inch, is nearly one-thousandth of an inch; whilst double the distance between the chord and the arc is not one fifty-thousandth."

In the early observations of Kater, he used a wood surface for a support, but later he seems to have preferred a marble slab, which, however, was not planed.

In 1844 Sir George Airy showed that, if  $n$  represents the number of supports of a bar, the distance between the supports should be

$$\frac{\text{Length of bar}}{\sqrt{n^2 - 1}}$$

in order to neutralize the effect of the flexure. Thus, in the case of the yard, if the defining lines are near the ends of the bar, each support should be placed 10.39 inches from the centre, and in the case of the meter they should be placed 28.87 centimeters from the centre.

This general form of support was used by Mr. Sheepshanks in all of his observations, and it is the form which is ordinarily employed at the present time. In the construction of the National Standards it was considered important that the bars should be supported at numerous points in order that they should be exposed to as little strain as possible. The particular form of support finally adopted will appear from the following description by Sir George Airy, to whose suggestion it is due.

"Great facility is given to the arrangements for supporting a bar with definite pressures applied at special points, by the use of levers. Thus, if any portion of the bar rest upon two rollers which are placed at the ends of a lever, and if the fulcrum of this lever (whether movable or not) be in its centre, the pressure upwards produced by these rollers will necessarily be equal. If there be another such lever, and if the fulcrum of this and the former be upon the extremities of a third lever, and if its fulcrum be at its centre, then the pressures upward produced by the four rollers will be equal. By this arrangement of the rollers and levers, one half of the bar may be supported. If another similar system be applied to support the other half of the bar, the pressures produced by its four rollers will also be equal among

themselves; and if the bar be laid symmetrically upon them, all the individual pressures will be equal." \*

Mr. Baily decided upon the adoption of eight rollers for the support of the National Standards, requiring for the distance between each roller and the one next adjacent  $\frac{86}{\sqrt{63}}$  inches = 4.54 inches. As a further precaution, the defining lines were traced upon gold plugs inserted in wells sunk to the plane of the neutral axis. This form of support is the one now employed in the Standards Office. The reader who desires to pursue this subject will find elaborate discussions by Bessel and by Clarke.

At the International Bureau only two supports are used, the distance between them being determined by Bessel's formula. At the Conservatory, the bars are placed directly upon a plane surface, which is nearly in the neutral axis of the support itself.

In 1876 Professor Wild proposed a form of support which seems to leave very little to be desired. The bars are placed *one above the other with the graduations in the same vertical plane*. Here we have conditions quite unlike those which occur with bars supported in the way already described, and under which it would seem that no flexure can occur which will affect the distance between the defining lines. This method, therefore, affords a rigorous test of the flexure formulæ of Bessel and Airy. It appears from the discussion of Professor Wild, that, while the mean effect of observed flexure upon the relative lengths of the separate decimeters of the same bar agrees nearly with the mean computed value, the numerical mean of the differences between the observed and the computed effects is no less than 0.0004 mm., or nearly one half of the whole mean effect. On the other hand, a rigorous comparison instituted by Clarke showed a substantial agreement between the computed and the observed effects of flexure. It is evident, therefore, that this subject requires further investigation. In the case where eight, or even four rollers are employed, it is mechanically impossible to make them so that planes tangent to each roller shall fall in a common plane, which shall be parallel with the plane of the defining lines. Unless this takes place, the upward pressures will not be equally distributed, and the formulæ will not hold. In the case of bars of the Tresca form, I am compelled to admit that, at least with a bar of copper, attention must be paid to the form of the support.

In the comparator which has been constructed from designs furnished by myself, I have dealt with the question of supports in the

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\* Astron. Trans., xv. 157, &c.

following way. The bed of the comparator is made of cast-iron, and is sixty inches long by fourteen inches wide. It has an extreme depth of two inches. In the centre, V-shaped ways run the entire length of the bed, upon which a plate carrying the microscopes, slides. The bed has at one end the means of bringing it into a horizontal plane, and at intermediate points screws for taking up the flexure. For this purpose, free vertical bolts, pressed upwards by means of levers and controlled by weights, are without doubt better than screws.

It is now necessary to provide for the movement of the microscope slide in a horizontal plane. This is accomplished in the following way. A shallow dish of mercury is placed upon the bed of the comparator, extending along its entire length. An arm projects from the microscope plate, to which is attached a plate sliding between guides, and carried by a micrometer-screw. To the lower part of this slide a platinum point is attached. One wire of a battery having a single cell is attached to the platinum. Another is placed in contact with the mercury. A sounder is placed in the circuit. The microscope plate is moved to one end, and the platinum point is brought into contact with the mercury, the contact being indicated by the "click" of the magnet. The slide is then moved to the other end, which is elevated or depressed by means of the adjusting screws, till the platinum point again makes contact with the mercury. After one, or at the most two trials, it will be found that the two ends of the bed-plate are in the same horizontal plane. The microscope plate is now set at the middle of the comparator, and the amount of the flexure is measured with the micrometer-screw. After about one third of the measured amount has been taken up by means of the flexure screws, the entire operation is repeated. In this way I find that the microscope plate can be made to move sensibly in a true plane. In practice, it is found that almost equally good results can be obtained by directly observing the surface of the mercury, with an objective of pretty high power, using the interior illuminator. The surface of the mercury admits of nearly as sharp a focus as the surface of a metal bar. Good results have also been obtained by dropping fine threads of spun glass upon the surface of the mercury. This method is rather more convenient than the method by contacts, but the latter admits of somewhat greater precision. From a limited number of trials, I conclude that contacts can be made with a probable error of a single contact not exceeding .00002 inch.

Knowing that the microscope plate moves in a true plane, the sur-

face of the bed-plate on either side can be brought to a plane which shall be parallel with that through which the microscope moves, by working it down till every part remains in the same focus. The bars to be compared are placed directly upon the surface thus prepared.

(d.) *The form and material of a bar which is best adapted to fulfil all the conditions which are essential to success in comparisons extending over a long period of time.*

In general, the form of a standard bar should be the same as that with which it is to be compared. For example, if one desires a standard yard which is to be compared with "Bronze 11," at Washington, the bar should be made of Baily's metal, and should be one inch square and about thirty-eight inches long. Kater preferred a thin bar. A width of one centimeter with a depth of three centimeters will be found to yield good results when the bar is placed upon a flat surface. Of all the forms proposed, that of M. Tresca, which has been adopted by the International Commission, seems to me the best designed to overcome all the difficulties of the problem. It is convenient to handle; it retains its form under its own weight, and quickly answers to a given change of temperature. I have had the pleasure of using a bar of this form for several months with the most satisfactory results. I began with considerable prejudice against it, influenced to some degree by a remark made by Professor Wild concerning it. It is undoubtedly somewhat difficult to manufacture, and will probably be found to be rather costly; but these are the only serious objections that can be urged against it. I express the opinion that it is well adapted to scientific work of the highest order. For use with my own bar, I have had constructed a special objective provided with an interior illuminator. The working distance is just sufficient to allow the passage of the bar under it.

(e.) *The investigation of the error due to the horizontal curvature of the ways of a longitudinal comparator.*

If the microscopes are stationary, and the bars to be compared are brought in succession under them, the curvature of the ways will produce no effect; but when the relation between the separate subdivisions of the given unit are to be investigated, or when a given length is to be transferred from one bar to another, the error arising from the curvature of the ways cannot be neglected. The comparisons of Troughton, of Hassler, and of Bache are subject to this class of errors, though of course it might have happened that in each case the curvature of the ways was insensible. I cannot find that any observations were made to determine the amount of the curvature. By reversing the position



of the bars to be compared, the error due to curvature will be eliminated in proportion to the ratio between the length of the chords described by the microscope for the two positions of the bars.

The necessity for taking into account the error due to curvature in any given case will clearly appear from the following provisional investigation of its magnitude in my own comparator:—

O A =	—3.8 cm.	A ———	<i>a</i>
O B =	+3.8	O ———	<i>o</i>
O C =	+23.8	B ———	<i>b</i>
O D =	+26.8	C ———	<i>c</i>
O E =	+30.6	D ———	<i>d</i>
		E ———	<i>e</i>

A steel meter by Froment was placed in the constant position O *o*. A copper meter of the new form by Tresca was placed successively in the positions A *a*, B *b*, C *c*, D *d*, and E *e*. The microscopes were attached firmly to the plate, moving freely upon the ways of the bed-plate, each having its own adjustment for focus. Microscope B was adjusted for coincidence with the end line of the bar O *o* at O, and microscope A was at the same time adjusted for coincidence with the end line of bar A *a* at A. The plate was then moved along the ways until microscope B was adjusted on the terminal line at *o*, and for this position the micrometer of microscope A was read. Since the two microscopes remain in the same position with respect to each other, the difference between the two readings of A will indicate the difference between the length of the bars. By reading B for the positions O *o*, —A being a constant,—the relation between the two bars will be expressed in terms of the micrometer of B also.

*Differences in the Apparent Length of the Bars compared, varying with the Position of Bar A with respect to Bar B.*

	Divisions of Micrometer.		Divisions of Micrometer.	
	From Microscope A.		From Microscope B.	
O-A =	—17.7	—9.0 $\mu$	—102.0	—9.1 $\mu$
O-B	+13.3	+6.7	+80.3	+7.1
O-C	+83.3	+42.1	+474.0	+42.2
O-D	+96.4	+48.8	+553.7	+49.3
O-E	+112.4	+56.9	+635.0	+56.5

For the radius of curvature, we have approximately,

$$.00658 : 34.4 = 100 : x.$$

$$\therefore x = 5228 \text{ meters.}$$

It is apparent, therefore, that, though the radius of curvature exceeds a distance of three miles, a correction of 3.8 divisions must be applied to the reading of microscope A, and of 21.4 divisions to the reading of microscope B, for each centimeter of the distance between the two bars.

The radius of curvature can also be found in the following way. If a tracing apparatus is attached to the microscope plate, a line traced upon the plane surface of a bar, by the motion of the plate from one end of the bed-plate to the other, will have the curvature due to the distance of the ruling diamond from the centre of the slide. If the bar is reversed, and a second line is drawn upon the same surface as nearly parallel to the first line as possible, then the ver-sin of the curvature will be equal to one half the difference between the distance of the lines at the middle point and the half sum of the distances at the two ends.

Finally, the deviation of the microscope plate both from a horizontal and from a vertical plane can be detected by means of a telescope mounted upon the sliding plate. If the telescope is pointed either at the cross wires of a collimator, or at a distant object, and the point remains fixed with respect to the cross wires of the telescope during the motion of the slide from one end of the comparator to the other, it may be assumed that it moves in an invariable plane. The longitudinal comparator at the Conservatory is provided with an attachment of this kind.

*(f.) The relative advantages of comparisons in air and comparisons in a liquid.*

Air temperatures are employed both at the Conservatory and at the International Bureau. At the Conservatory, the bars to be compared remain at a constant air temperature for forty-eight hours before the comparisons are made. The arrangements for maintaining a constant temperature are most admirable and effective. The means of controlling the temperature employed at the International Bureau are somewhat different, but they give most excellent results. Nevertheless, it is yet an open question whether the absolute relation between two bars compared in air at a given temperature can be made to agree with the absolute relation determined by submerging them in a liquid at the same temperature. The writer has met with many difficulties in this direction.

*(g.) The variation of the absolute length of a bar by a change in its molecular structure or otherwise.*

There are some evidences that certain standards have undergone a

change of length since their original construction, but in no case does the evidence seem to me to be conclusive. It is understood that Colonel Clarke finds a well-defined change in some of the standards originally measured in 1842-55. The platinum meters of the Royal Society present some evidences of a change of length *inter se*.

According to the Fifth Report of the Standards Commission (Appendix), we have the Royal Society end-meter equals:—

Royal Society line-meter	+0.01759 mm.	(Arago, 1818.)
“	“	+0.01881 (Kater, 1818.)
“	“	+0.00940 (Baily, 1835.)
“	“	+0.00837 (Standard's Office, 1869.)

We have here an appearance of a change. In deciding whether it is a real or an apparent change, it should be remembered that in 1818 there was no defining cross-line on the line-meter, and that there is no existing data by which the accuracy of the constants of the contact pieces used with the end-meter can be estimated.

The Russian standard of length used in the geodetic surveys previous to the work done by Prazmowski and Wagner presents the most authentic instance of a well-defined change of length which has come under my notice. This bar is made of iron, and has a length of seven feet. I am not certain whether it was forged or drawn through dies. Conical end-pieces of tempered steel were inserted in each end. In the course of two or three years, this bar was transported a distance exceeding 8,000 miles, being supported in a packing of feathers. At the end of this time it was found by Prazmowski to be one thirteenth of a line, or about .006 inch shorter than at the commencement of the expedition, the two sets of comparisons having been made at the same temperature.

If it can be established that no permanent flexure of the bar took place, we have here an authenticated instance of an actual change of length. Upon the discovery of this change, from whatever cause produced, a new standard was constructed, also made of iron. It was allowed to anneal for eight days after being forged. It is understood that no change of length has ever been detected in this bar. Against this somewhat doubtful evidence we have the positive evidence by Chisholm, that Bronze No. 6 showed no evidence of a change in length in 14 years, and of Baeyer that the precise mean length of Bessel's standard bars at 13° Reaumur had not altered in the 20 years from 1834 to 1854. The change in the mean length is to be distinguished from a change in the coefficient of expansion. The evidence of Baeyer

seems tolerably conclusive that bars of iron and zinc are liable to suffer a change in their coefficients of expansion, either by an actual change in their molecular structure or by the action of external causes.

The continuous measurements of the Conservatory and of the International Bureau will, in the course of the next decade, furnish data which will add much to our knowledge of this subject.

(h.) *The law which governs the expansion of bars of different materials, and having different masses, under a varying temperature.*

It is well known that Mr. Sheepshanks, in the comparison of "Bronze bar 28 with Cast-steel bar D," near the close of his labors on the National Standards, found deviations which he could not explain. The importance of this matter justifies me in quoting in full the statement of Sir George Airy in his account of the construction of the national standards.

"I proceed now to allude to a discordance which was a source of great anxiety to Mr. Sheepshanks.

"In April, 1855, Mr. Sheepshanks was engaged in measuring the bar Cast-steel D. By comparisons with four iron bars, (as stated in the table above,) whose results agreed very closely, the excess of Cast-steel D above Bronze 28 was found to be  $-8^d.61$ . But a direct comparison of Cast-steel D with Bronze 28 immediately preceding had given  $-0^d.46$ . This comparison was made at the temperature  $45^{\circ}.54$ , or  $16^{\circ}.46$  below the standard temperature. A trifling error of expansion might account for part of the discordance, and the ordinary errors of observation might account for part. But in the opinion of Mr. Sheepshanks, though the whole discordance scarcely exceeded the effect of the thermometric expansion of Bronze 28 for  $0^{\circ}.3$  Fahrenheit, it was impossible so to explain away the whole or a large part of it; and he was convinced that Bronze 28 had sensibly shortened. And so deeply and so painfully was this impression fixed in his mind, that he actually contemplated the rejection of all the results which had cost so many years of labor, and the commencing the work *de novo*."

Mr. Sheepshanks first disproved, by observation, the first conjecture on the possible cause of the apparent change; viz. "that Bronze 28, still covered with gold-beater's skin and cement (as in the earlier comparisons), might have been so constrained by that covering that it could not shrink down to its natural length; but that in the last comparisons with Cast-steel D, when that covering had been removed, it had contracted itself."

He then compared Bronze 28 with twenty-seven different bronze bars, and by comparing the old and the new measures found, with only

one exception, a very close accordance. Mr. Airy concludes this part of his report as follows:—

“First, there is no evidence whatever of a general preponderance of excess from the New Measures above the excess from the Old Measures; the signs + and — being intermixed, in the differences, in all possible ways, and the mean of the whole being less than  $0^d.50$ . Secondly, the only instance which fairly supports the conclusion deduced from Cast-steel D is the first of all, namely, Bronze 12. Cast-steel D was compared on April 13, 14, and 16; Bronze 12, on April 26, 27, 28, and May 1; Bronze 39 (the next), on April 30. The conclusion, I think, is inevitable, that Bronze 28 really was shortened at the beginning of April; that it recovered its exact length before April 30; but that this recovery took place with some fluctuations, so that on May 1 it was subject to nearly the same error as before. Bronze 21, observed June 26, exhibits a similar discordance. What circumstances can have produced these changes, or how far the later fluctuations are apparent rather than real, I am wholly unable to conjecture.”

I believe that the explanation of the phenomena observed by Mr. Sheepshanks will be found to fall under the following:—

*First, two bars of different materials, having different shapes and different masses, have a variable coefficient of expansion with respect to each other, which is a function of the time of exposure to a given temperature.*

*Second, the more violent the change of temperature, the greater will be the variation in the length of the bars before they assume their normal condition under a constant temperature.*

All of the bronze bars had the same mass. The iron bars and the steel bars, on the other hand, not only had a different mass, but they were subject to a different degree of specific heat. Their conductive power was also different. They also had a different absorptive power. The difficulty with the observations of Mr. Sheepshanks was, that they were not sufficiently continuous. They did not extend over a sufficient length of time to enable him to discover the slow changes which were going on in the length of the bars through the heat already absorbed, and *which was not indicated by his thermometers.*

This paper has been already extended so far beyond the limits proposed that it is inexpedient to give even a *résumé* of all the observations which I have made bearing upon this point. It will be seen from the following brief account, that it is absolutely necessary to investigate the performance of two standards which are to be compared un-

der the action of a varying temperature, in order to decide how long they must remain at nearly a constant temperature before comparisons can be safely made. The comparing-room is a small triangular space partitioned off from the cellar of the west wing of the Observatory. It has two windows, one facing south and the other west. All the heat of a furnace can be turned into the room through a pipe entering it near the ceiling. The comparator is mounted on brick piers insulated from the building. The temperature of the room can be considerably reduced by means of two refrigerators, supported near the ceiling. Centigrade thermometer No. 1 is imbedded in the base of the comparator, and packed with iron filings taken from the bed-plate. Centigrade thermometer No. 2 is suspended by a fine wire about half-way between the point where the heat from the furnace enters the room and the upper surface of the comparator.

Series I. consists of partial records of a comparison of a line-measure steel yard by Troughton and Simms with a yard laid off on platinum-iridium plugs inserted in the bed of the comparator. Series II. consists of partial records of a comparison between two line-measure steel bars, of which one is nickel-plated, the graduations being upon the nickel surface. These two bars were made at the same time, and of the same material. The bars have the following dimensions:—

	Length.	Breadth.	Depth.
* Nickel-plated bar,	40.4 in.	0.5 in.	2.0 in.
Steel bar,	89.87	0.6	1.6

A thin vertical lamina of platinum is inserted in the shorter bar. In other respects, it differs from the longer bar only in its dimensions, and in not being nickel-plated.

After the bars were placed in position, they were not disturbed till the close of the observations. Whatever changes took place, therefore, were due entirely to the action of temperature upon the bars. In Series I. the value of one division of the micrometer employed was .0000035 inch. In Series II. it was .0000197 inch, as stated on page 291.

#### SERIES I.

	Time.		Thermometers.		Diff. in Length in Divisions of Micrometer.
	h.	m.	No. 1.	No. 2.	
1880, Mar. 22,	9	45 A.M.	5.7	—	+35.6
	9	48	5.9	—	+35.8
	9	50	6.4	—	+40.7

Closed windows, and turned on heat.

	Time.		Thermometers.		Diff. in Length in Divisions of Micrometer.
	h.	m.	No. 1.	No. 2.	
1880, Mar. 22,	9	54 A.M.	6.7	—	+54.2
	9	57	6.8	—	+69.1.
	9	59	7.6	—	+77.0
	10	2	8.3	—	+97.8
	10	4	9.0	—	+116.3
	10	7	9.4	—	+136.4
	10	11	10.0	16.7	+158.1
	10	15	11.0	19.4	+197.4
	10	18	11.4	20.6	+218.5
	10	20	11.7	21.1	+238.5
	10	23	12.2	22.2	+260.0
	10	26	12.5	22.5	+280.8
	10	28	12.8	23.3	+300.8
	10	30	13.1	23.9	+328.8
	10	32	13.4	24.0	+347.1
	10	35	13.9	24.9	+369.6
	10	38	14.2	25.0	+389.8
	10	41	14.7	25.6	+404.0
	10	43	15.1	26.2	+423.8
	10	46	15.3	26.7	+443.0
	12	0	20.3	33.3	+660.1
	0	4 P.M.	20.4	33.2	+659.7
	0	46	25.5	34.4	+615.9
	0	49	25.7	—	+611.7
	1	46	29.2	35.6	+550.6
	1	49	28.9	35.6	+537.9
	2	5	29.6	—	+499.9
	5	53	38.8	—	+50.2
	6	1	38.3	—	+31.1
	6	3	38.2	—	+23.0
	6	7	38.3	—	17.0
	7	18	38.8	—	+2.4
	7	50	38.8	—	—1.6
	8	21	38.8	—	—1.2
	8	37	38.8	—	—4.8
	8	39	38.8	—	—9.1
Mar. 23,	6	28 A.M.	5.0	—	—167.1
	6	30	5.4	—	—165.8
	6	50	7.3	—	—132.2

	Time.		Thermometers.		Diff. in Length in Divisions of Micrometer.
	h.	m.	No. 1.	No. 2.	
1880, Mar. 23,	9	7 A.M.	9.9	—	+62.9
	10	47	11.6	—	+19.4
	7	58 P.M.	19.0	—	—86.5
	8	1	19.1	—	—81.8
Mar. 24,	6	44 A.M.	17.5	—	—147.2
	7	51	17.2	—	—150.4
	8	54	17.2	—	—149.9
	8	57	17.2	—	—151.8

## SERIES II.

	Time.		Thermometers.		Diff. in Length in Divisions of Micrometer.
	h.	m.	No. 1.	No. 2.	
1880, April 11,	4	33 P.M.	47.7	51.1	—297.3
	4	35	47.7	—	—296.5
	4	37	47.7	50.8	—295.0
Shut off heat, and opened windows.					
	4	43	—	—	—288.1
	4	47	46.8	23.0	—327.0
	4	49	45.0	19.2	—420.3
	4	52	44.4	19.1	—464.1
	4	55	43.8	18.9	—535.7
	4	59	42.8	19.0	—580.7
	5	1	41.0	19.0	—638.1
	5	5	40.2	19.0	—669.5
	5	9	—	—	—702.1
	5	10	—	—	—707.7
	5	13	38.3	20.0	—716.0
	5	27	36.0	21.0	—742.5
	5	32	—	—	—746.7
	5	36	34.0	20.3	—741.2
	5	41	—	—	—780.7
	5	46	33.6	19.2	—694.5
	7	35	24.1	17.8	—497.1
	10	5	8.2	4.4	—453.9
April 12.	Windows open all night.				
	6	46 A.M.	1.2	1.3	—374.3
	7	18	2.7	1.1	—369.6
	8	7	1.8	1.7	—363.9
	2	34 P.M.	4.6	6.2	—311.6



	Time.		Thermometers.		Diff. in Length in Divisions of Micrometer.
	h.	m.	No. 1.	No. 2.	
1880, April 12,	4	46 P.M.	6.7	9.8	—283.0
	8	30	8.2	7.9	—360.7
	8	33	8.2	7.9	—364.9
	10	20	7.2	6.3	—386.5
	10	35	7.1	6.9	—376.5
	10	56	7.1	7.0	—376.2
	11	25	6.6	6.1	—378.0
	12	16	6.2	5.2	—372.0
April 13.	Windows open all night.				
	6	53 A.M.	3.1	3.9	—329.4
	6	59	3.1	3.9	—326.9
	8	23	4.1	6.0	—302.0
	8	26	4.1	6.0	—296.1
	8	33	4.3	6.9	—290.2
	9	13	5.2	8.2	—266.7
	9	15	5.2	8.2	—268.5
	10	6	6.9	10.2	—243.5
	10	8	6.9	10.2	—246.3
	11	37	9.7	13.0	—247.9

If the changes of temperature are gradual, the two steel bars will reach a state of rest under a constant temperature in about twelve hours; but if they are subjected to an abrupt and violent change of temperature, it is not safe to make the comparisons till after the lapse of from forty-eight to sixty hours.

Baily's comparisons of the yard of the Royal Society certainly show traces of an error of the kind I have here described. On the other hand, Clarke's comparisons do not show any marked evidence of their existence. But in the former case, the comparing-room was not well adapted to the maintenance of a steady temperature, while in the latter it appears to have been admirably constructed. As observations are still being made with the apparatus at Southampton, it would be interesting to see if results corresponding in a general way with those I have found could be obtained from a special series of comparisons arranged for this specific investigation.

An investigation of the character which I have indicated is especially necessary in the measurement of base lines in which the standard unit is necessarily subject to greater and more rapid variations of temperature than take place in a well arranged and protected comparing-room. Still further observations are necessary in order to determine

whether end-measures behave in the same way as line-measures under a varying temperature.

(i.) *The exact relation between the length of the Imperial Yard and the Meter of the Archives.*

The Imperial Yard has never been directly compared with the Meter of the Archives. Our knowledge of the value of the equation between these standard units depends solely upon, —

*First.* The indirect comparison of the platinum meters of the Royal Society with the Meter of the Archives by Kater, Baily, Clarke, and Chisholm. All these determinations rest upon the relation of the Royal Society platinum meters to the Meter of the Archives given by Arago in 1818.

*Second.* The comparison of the iron meter of the United States Coast Survey with Troughton's scale, by Hassler (27<sup>in</sup>. — 63<sup>in</sup>.) in 1832.

The following are the relations given by the authorities named above. I have subtracted .00087 inch from the value given by Hassler, this being the amount by which the yard on Troughton's scale exceeds the length of "Bronze 11" when reduced to 62°.

Kater, 1818,	"Mètre à Traits "	= 39.37076 inches.
	"Mètre à Bouts "	39.37081
Kater, 1820,	Dolland's Scale	39.37045
Baily, 1836,	"Mètre à Traits "	39.36968
	"Mètre à Bouts "	39.36937
Clarke, 1866,	"Mètre à Traits "	39.37048
Chisholm, 1870,	Standard Meter on Baily's metal	39.37112
Hassler, 1832,	Original Iron Meter	39.38005

Mr. Hassler compared several other standards with Troughton's yard, but they are not included in the above table; first, because, with the exception of the brass meter by Lenoir, there is no evidence that the standards compared are authentic copies of the original; and, second, because the certificate of the meter by Lenoir refers to the Meter of the Observatory, and not to the Meter of the Archives.

It is obvious from this table, that our present knowledge of the relation between the length of the yard and the meter is subject to great uncertainty. In deciding upon the weight which should be assigned to any particular value, it is to be remembered, —

(a.) That in the comparisons by Kater, Baily, Clarke, and Chisholm, the constant relation given by Arago is subject to great doubt.

(b.) That the meters of the Royal Society do not admit of exact measurements in their present state.

(c.) That Kater has himself declared his own determination to be erroneous.

(d.) That the values given by Baily are expressed in terms of the Scale of the Astronomical Society, which for 39.37 inches is .00076 inch *longer* than the Imperial Yard.

(e.) That the value given by Mr. Chisholm involves the errors of transfer to the bar of Baily's metal.

(f.) That the lines on the bar of Baily's metal do not admit of great precision in comparisons with moderately high powers.

(g.) That the original iron meter has never been compared with the Meter of the Archives, but only with the Meter of the Conservatory.

In view of these facts, it does not seem too much to say that it is at present impossible to assign any value to the equation between the yard and the meter, which is not liable to an error as great as .005 inch.

Finally, the confusion with regard to this relation has become so great, that, by an act of Parliament passed in 1878, the relation found by Kater was declared to be the legal relation, without regard to the various determinations which have since been made.

I will close this article with an abstract from the Philosophical Transactions for 1798, p. 180, giving the errors of the six-inch spaces of Troughton's scale as determined by Shuckburgh. As this scale is understood to be still in existence, it would be interesting to have a remeasurement of these spaces with a comparator of modern construction. I know of no modern graduations which have a much greater apparent accuracy than is here indicated.

Inches.	Error, or Difference from the Mean.
0 to 6	+ .00012 inch.
6 to 12	+ .00000
12 to 18	+ .00007
18 to 24	— .00013
24 to 30	— .00006
30 to 36	+ .00020
36 to 42	— .00033
42 to 48	+ .00007
48 to 54	— .00003
54 to 60	+ .00010

HARVARD COLLEGE OBSERVATORY, April 14, 1880.

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## XVI.

THE COLUMNAR ARCHITECTURE OF THE  
EGYPTIANS.

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Presented May 12th, 1880.

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I. THE DERIVATION OF THE DORIC ORDER FROM EGYPTIAN  
PROTOTYPES.§ 1. *Introductory.*

In the following essay I have attempted a slight examination of the well-known archæological question, Was the Doric Order imported into Greece from Egypt? in so far as that question is illumined by an investigation into the theoretic origin and development of the column and the pier as architectural members. The chronological, geographical, and politico-historical elements of the problem are for the time forgotten, and the attention fixed on the comparative artistic value and significance of the so-called "proto-Doric" pillars in Egypt and the columns of the Doric style in Greece, as capable of bearing important testimony to the actual connection between the two. In the present state of our knowledge this method of attacking the

question seems to me to be the only one that leads to even measurably certain conclusions.

My plan is first to state the outlines of the theory of the column and the pier, and then to attempt to apply that theory to the elucidation of the forms in question.

## § 2. *Theoretical Origin of the Column and Pier as Architectural Members.*

A COLUMN, as I shall use the term, is a free, vertical architectural support or prop, whose transverse section is either a circle, a modified circle, or several circles grouped together. It is *free* in that it is unconnected with the building to which it belongs, except by its mechanical bearings, namely, its two ends. This separates it from the pilaster and the vertical moulding. Its *verticality* distinguishes it from the flying buttress and rafter. As a *support* for the entablature and roof, it is distinct from all tower, obelisk, and mast forms, the column being always more or less subservient in the conformation of its summit, and of the lines and decorations of its parts, to the superposed structure, while the spire or obelisk is entirely self-determined. The section of a column is a simple, modified, or compound *circle*; as, for example, simple in Tuscan, modified — by flutes — in Doric and Corinthian, compound in some Gothic columns. This characteristic keeps it apart from the pier.

A PIER is a support, free and vertical like a column, but one whose transverse section is a simple, modified, or compound *rectangle*. A square pier, so long as it has neither base nor cap-stone, is simply a wall whose length equals its thickness. Regarded in this light, therefore, in addition to its supporting intent, it has an object entirely foreign to a column, namely, the limitation of a space. The rectangular form, however, may be reached from a slightly different starting-point. In rocky excavations it is necessary to leave pillars at intervals to prevent the collapse of the roof. These pillars are ordinarily quite carelessly shaped, but the first step toward an architectural form is the reduction of their rough masses to plane-bounded piers.

At all events, the pier and the column are of widely different origin. While the former is to be regarded as the descendant either of a wall or of an underground pillar, the latter must in the last analysis be traced to the wooden prop of a primitive hut. The pier, in short, is of mineral, the column of vegetable origin.

The pier, it is true, may receive a cap-stone and base, its angles

may be replaced by planes, — making it polygonal; yet, though it may thus acquire features like those of a column, its essential character remains entirely different. Even if, by continuing the process of replacement, a pier were produced with an infinite number of sides, and with a transverse section sensibly coinciding with a circle, and so, to mere scientific scrutiny, it were transformed into a cylindrical column, it would fail of being a column in any true, philosophical sense. Conversely, a column may lose its distinguishing characteristic, may be planed down to prismatic angularity, and yet continue to demand of the critic the same treatment as before. In short, the lines of development which start from the primitive pier and the primitive column may approach indefinitely, but, strictly speaking, can never meet.

### § 3. *First Steps in the Development of the Column and Pier.*

The only indispensable member of either column or pier, as well as the one that especially proclaims the type of each, is the shaft, — an upright beam or pillar to convey the roof-weight to the floor. Since, however, in simple huts, a wooden prop resting on a damp floor is likely to decay, or, if small, to be crowded into the ground, a very natural and early improvement is the insertion of a flat stone beneath it, to prevent one or the other, or both, of these mishaps. This flat stone is the primitive plinth. Again, in order that the roof-beams may rest more firmly on the head of the prop, a flat, plinth-like slab is perhaps placed on its top. In case the potential column be composed of bamboos or reeds tied together in a bundle, — as often in alluvial countries, — such a cap is almost necessary. This tile or block, for whatever purpose designed, is the primitive abacus. Now, when the growing desire for neat and tasteful construction demands the exchange of the scraggy prop for a straight, carefully chosen log, and when this log is trimmed and smoothed, these supplementary members are squared to correspond with the increased elegance of the shaft. Furthermore, when in process of time the wooden support is copied in more or less durable materials, as sandstone or marble, the plinth and abacus, though no longer of such obvious necessity, are often retained for reasons of taste. The plinth is kept not so much because the architect fancies that the marble shaft is in any sense subject to decay, or even because a suitable platform is lacking to sustain it, as because, when lifted and planted on a sort of pedestal, it *looks* more stable, *seems* to spring more satisfactorily from the undefined level of the floor. Simi-

larly, the abacus is kept not only because the architrave is really better provided for with it, and the shaft itself better defended against the hostility of the elements, but also because with it the support *seems* more ample, the protection more complete, and because by it the beauty, individuality, and dignity of the shaft are decidedly enhanced. The mechanical reason for the expansion of the upper part of the shaft into an echinus or capital is not so easy to discover. It seems necessary to consider the motive almost entirely æsthetic. To be sure, the strength of the abacus is greater if its projection beyond the limits of the top of the shaft be slight, and, where convenience requires a slender column, this strength is most easily obtained by widening the upper end of the shaft until it approaches the dimensions of the abacus. But just what natural form is employed for this purpose is very doubtful. On the other hand, this addition is entirely explicable from the side of æsthetics. The increased beauty of the shaft, the extended facilities for varied decoration, and the closer union of shaft and abacus, are obvious. Finally, a simple expedient to prevent the chance splitting or separation of the primitive prop or reed-bundle is, of course, a thong, cord, or ring bound around its top. Hence arises the astragal.\*

It is an important fact, worthy of mention at this point, that in Egyptian architecture the abacus is properly not a part of the column, but a projection from the architrave. In this particular the architecture of Egypt is contrasted with that of Greece.† In the former the column is terminated by its capital, in the latter by its abacus. The Egyptians, therefore, seem to have regarded the column as a more independent member than the Greeks, and so to have crowned it with its most prominent and beautiful part. Hence, an Egyptian column might be tolerated without any incumbent weight, while its Greek homologue without an entablature would be as meaningless as an unresolved chord of the seventh.‡

As the difference between column and pier is perhaps not generally admitted or understood,§ and as the modified forms of the two

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\* For a trace of the primitive form of the astragal in Greek architecture, see Paus. v. 20; and also, upon the same, Wilkins, Athens, p. 18, note.

† Schnaase, *Gesch. d. bildenden Künste*, i. 386.

‡ Another indication that the Egyptians had no such delicate sense of the supporting function of the column as the Greeks is to be found in the frequency with which they nullified the idea of verticality by the use of *horizontal* zones of color on the shaft and capital. See Schnaase, *op. cit.*, i. 330.

§ For instances of the same use of terms as that found in this essay, however, see Gwilt, *Dict. of Architecture*, p. 735, and Müller, *Anc. Art and its Remains*, tr. by Leitch, pp. 308, 309.

approach each other so closely that serious confusion has arisen about them in architectural criticism, it seems necessary to attempt to give an outline of the theoretical development of the latter type with much the same fulness as of the former. A few examples, taken, for various reasons, almost exclusively from Egypt, will also be adduced by way of illustration.

The primitive pier, occurring, as has been said, in caves, is of necessity so shapeless, so entirely the product of utilitarian selection, that except by a stretch of language it cannot be brought within the jurisdiction of art history. The first excavations in rock follow the veins or strata that can be cut into with the least labor. They are irregular and rambling,—now constricted into galleries, now expanded into chambers. Hard spots are avoided, cut around, and left. Wherever large rooms are desired, some kind of pillar is allowed to remain to keep the roof from tumbling in. Any large coal-mine will furnish abundant instances of this primitive use of the pier.

When now the artistic instinct begins to assert its authority, and demand that these excavations, whether or not used for habitation, be made more neat and attractive, the walls, roof, and pillars are smoothed, and made to conform to some definite lines. A rectangular shape is chosen for the cave, which is as large as the consistency of the rock will warrant. If more space be called for, a second chamber is added to the first, separated from it by a partition, but communicating with it by a door. Presently it is observed that this partition-wall can be safely perforated by more than one door, and the conveniences of space almost doubled. The wall becomes a line of pillars of uniform depth or thickness, but very possibly of varying width. This stage of development is admirably exemplified by the ancient Tourah quarries,\* whence the stone for the Great Pyramid was taken, and by many of the tombs on the plateau of Gizeh. Among the latter are rectangular rooms of all sizes and shapes, with partitions entire, half broken up, or completely transformed into a row of piers.† Of later date, but nearly similar construction, are the Tombs of the Kings at Thebes.‡

Whether the next step be the decoration of the simple square pillar, or the addition of an abacus-like projection above it, is indifferent.

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\* Vyse, *Pyramids of Gizeh*, iii. 90–94.

† *E.g.*, Lepsius, *Denkmäler aus Egypten*, i. 26, 28, 29, Tombs 71, 88, 92, et *passim*.

‡ *Ibid.*, i. 96, 97.

The abacus probably first occurs in such half-excavated, half-erected structures as some of the tombs at Gizeh, which are cellars covered with a roof of dressed stone.\* The abacus in such cases is only a contrivance for collecting the roof-weight. In fact, in Egypt it frequently appears in such hybrid buildings, but not in genuine excavations like those at Tourah, Bab-el-Molûk, or Benihassan,† except with piers of a highly complex character. The decorations applied are determined by the intent of the excavation, and by the national genius for decorative art. A plain surface and a rectangular shape are among the earliest refinements of the jagged pillar. Inscriptions, rude outlines of pictures follow, and by gradual approaches such bas-reliefs are reached as those found in Tomb 90 at Gizeh,‡ or in Tombs 1 and 2 at Zauiet-el-Meitîn,§ where in the one case figures of men are inserted in the face of the pier, and in the other a beautiful little knot of lotus-flowers, with a papyrus-bell or two, is shown tied up by a cord, seemingly bearing on its apex the load of the ornamented architrave. The plinth, although an important member of columns, is not required by stone piers, especially when floor and pier are continuous. Hence, in the earliest Egyptian examples, it is not to be found.¶ At Benihassan, however, plinths are invariably present in the more elegant of the tombs, but accompanying highly developed piers. They belong to a time when the beauty and fitness of bases for columns have been acknowledged and conventionally adopted for piers also.¶

The pier idea has as yet progressed but a few steps. A new one is now very readily taken. The rigid angles of the square pier are broken by bevels beginning just below the upper, and ending just above the lower end of the pier. For an illustration, take Tomb 31 at Sakkarah, where four piers, notably *without abacus or plinth*, are adorned in this simple way.\*\* Now, continue these bevels upward and downward, and increase their surface until it equals that which

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\* Lepsius, i. 21, Tombs 15, 16, and 17.

† Ibid., i. 59, 60.

‡ Ibid., i. 27.

§ Ibid., i. 57; Schnaase, *op. cit.*, i. 384; Reber, *Kunstgesch. d. Alterthums*, p. 14.

¶ Tomb 24 at Sakkarah, which might at first sight seem to be an exception to this, is really very late, belonging probably to the time of Psammitichus, Dynasty XXVI. See Lepsius, i. 40; Wilkinson, *Anc. Egyptians*, ii. 262; Kenrick, *Anc. Egypt*, i. 259; Vyse, *Pyr. of Gizeh*, i. 218.

¶ Lepsius, i. 58-61; Rosellini, *Monumenti dell' Egitto*, ii. 1, 2. See also Essay II., § 4.

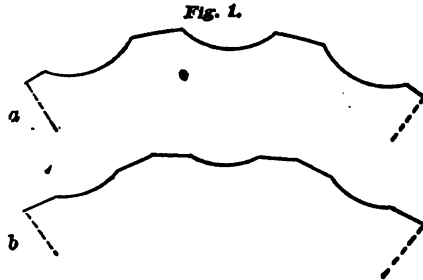
\*\* Lepsius, i. 42.

remains of the four original sides, and an octagonal pier results. By repeating the process of replacement, sixteen-sided and thirty-two-sided piers will be produced. Examples of the octagonal variety are found in the portico of Tomb 1 at Benihassan,\* and of the sixteen-sided in the interior of the same tomb, or in the portico of Tomb 2.†

The pier has now reached a stage of evolution at which its faces may be beautified by flutes. The flute may be applied either to columns or to piers. It is a very incomplex but effective device to diminish the cumbrousness of a shaft without diminishing its apparent strength, to adorn a surface otherwise plain or simply rounded by the changing grace of light and shade, and, by directing the eye irresistibly to the vertical lines, to render the supporting office of the shaft more obvious. Its origin is much disputed, and it may be more satisfactory to regard it as a merely fanciful decoration employed for the purposes just enumerated. However that may be, it is of cardinal importance for us to observe the forms that result from its use on columns and piers. Take, for example, a round wooden column, and at regular intervals introduce sixteen narrow vertical grooves into its sides; take also a sixteen-sided stone pier, and make a similar groove

in each of its sides,—and compare the results. In the first case a smooth convexity remains between the flutes; in the second, two narrow planes meeting in a sharp edge. But if the width of the flutes be sufficiently increased to make the edges of adja-

cent ones coincident, the whole surface of the shaft in both cases will be occupied by vertical concavities meeting in sharp edges, and it will be almost impossible to tell which of the modified forms originated in the cylinder and which in the prism; for their sections, if their diameters be the same, will be precisely alike. Now, if the modified column be copied into stone and set beside the modified pier, no difference in their shafts will be discernible; yet there is a difference, an



\* Lepsius, i. 60.

† Ibid., i. 59, 60; Rosellini, ii. 1, 2.

FIG. 1. *a.* Partial horizontal section of column with 16 flutes separated from each other by listels. *b.* Do. of pier with 16 fluted faces which meet in sharp edges between the flutes.

essential difference, a difference that criticism is bound to observe. Hence, in the discussion of the identity or non-identity of two such forms, the argument, if following this general direction, must turn upon the answer to the question respecting each, "Did the artist, consciously or unconsciously, work with the column or the pier type in mind?"

§ 4. *Application of the Theory to the "Proto-Doric" Question.*

Should we continue the study of the logical evolution of the column and pier, we should find the subject steadily becoming more clear, and the conclusions in regard to it more abundantly substantiated by familiar examples. But we have gone far enough for our purpose: let us now turn to the application of the theory to the actual forms before us. I have approached the criticism of the forms themselves by a circuitous route, because I am convinced that only thus can we see them aright. The famous question of the existence of Doric types in Egypt must be regarded from the side of theoretic development rather than from that of natural history; we must seek to determine the artistic motives, whether consciously operative or not, which directed architects in Egypt, and afterwards in Greece, in the choice and elaboration of the forms in question, rather than merely to compare their shapes and proportions as so many similar or dissimilar phenomena. Not that this scientific comparison is valueless, but that its conclusions are not so decisive as those which result from a thoughtful consideration of the early development of architectural ideas. Hence, though I shall refer to the external differences between the Egyptian and the Greek forms, I shall do so principally because they add something to the probability of the internal ones.

My purpose, briefly stated, is to show how I conceive that the true Doric and the so-called "proto-Doric" forms stand at the ends of two long lines of development that set out from totally diverse sources. No one, I think, will venture to argue that the forms under consideration are primitive or simple; they are rather elevated points in the course of artistic progress, which were reached, not by a sudden leap, but by gradual approach. If, then, though the points themselves seem to lie never so near together, the lines of development in which they lie can be traced backward towards their starting-points, and can be shown to be so strongly divergent when thus pursued that their origins cannot be identical, the irreconcilable theoretic separation of the points is established and their historic connection rendered improbable.



## § 5. "Proto-Doric" Forms in Egypt.

One of the *prima facie* objections to the "proto-Doric" theory is the extreme rarity of "proto-Doric" forms in Egypt. Were there

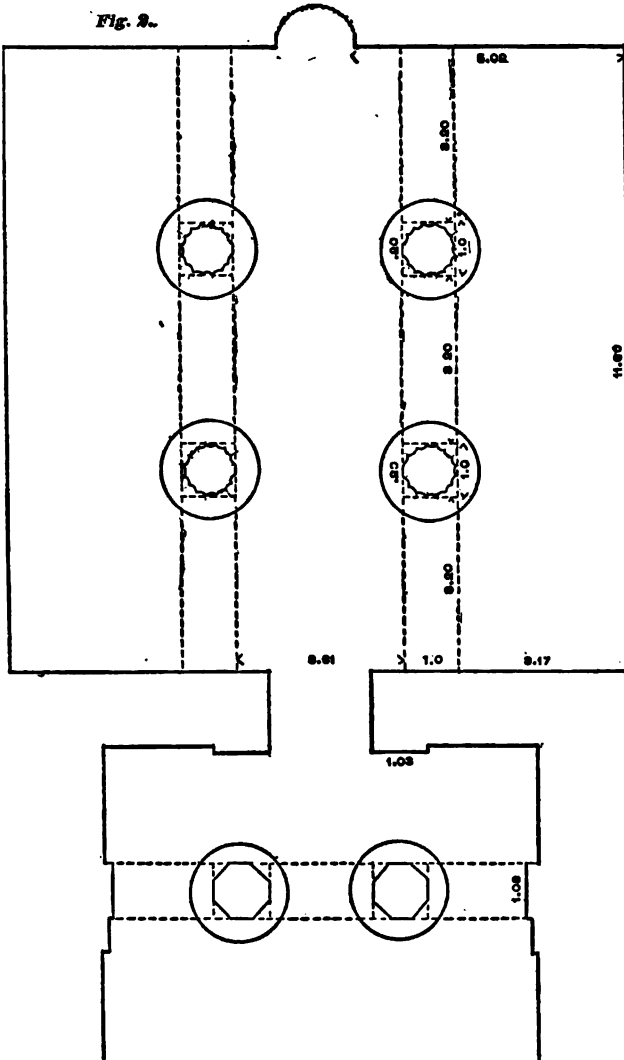


FIG. 2. Ground-plan of Tomb 1 at Benihasan, showing the plane faces left on the inner sides of the fluted columns, and the position of the architraves and abaci. (After Lepsius.)

any national order that the Greeks were supposed to have stolen, the case would be entirely different. But, so far from this, the "proto-Doricists" have had great difficulty in finding even a few good examples for their argument. Indeed, Mr. Falkener, who seems to have pursued the subject most enthusiastically in his "Museum of Classical Antiquities," (London, 1861,) was able to scrape together but a pitiful *twenty-seven*.\* I have been unable to gain access to Mr. Falkener's treatise directly, but my argument respects what the unanimous testimony of quotations and references in other books shows to be his strongest examples, namely, the Northern Tombs or "Grottos" at Benihasan.

As the curious traveller descries those rock-cut porticos on the eastern bluffs of the Nile valley, and notes the chaste and un-Egyptian simplicity of their graceful shafts, he may be reminded quite excusably of some Greek distyle cella *in antis*, and may infer, though not very logically, that therefore the world-renowned Greeks in their columnar architecture were only plagiarists from the Egyptians. In the path of this inference, as already repeatedly implied, stand several insurmountable obstacles; for the two species of proof referred to — external and internal — indicate that in respect of both outward appearance and inward motive the "proto-Doric" and the true Doric must be thrown into different categories. These two classes of proof I shall now proceed to state.

#### § 6. *External Differences.*

The differences that may be distinctively called *external* lie either in the dimensions of the forms, or in the number and character of the constituent members. Under the head of measurable differences may be classed the differences (1.) in the rate of diminution of the shaft, i. e. the ratio of the difference between the upper and lower diameters to the distance between the points at which those diameters are taken, or the height of the shaft; (2.) in the slenderness of the shaft, i. e. the ratio between its lower diameter and its height; and to these may be conveniently added, (3.) in the number of flutes or faces susceptible of fluting. Under the morphological differences, if we may call them so, are to be grouped (1.) the various members which the Greek order possesses, but the Egyptian lacks; and (2.) the one member which the Egyptian order has, but the Greek lacks.

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\* Fergusson, *Hist. of Architecture*, i. 220; Wathen, *Arts, Antiquities, and Chronology of Anc. Egypt*, (London, 1843,) p. 180.

The diminution of the Greek shafts is much more rapid than that of the Egyptian; and, furthermore, is generally more rapid in the older Greek temples than in the later. For example, I take a few specimens from the long list given by Dr. P. F. Krell, in his "History of the Doric Style" (Stuttgart, 1870):—

Temple at Assos . . . . .	1 in 11.62
Temple of Poseidon at Pæstum . . . .	" 13.34
Temple of Heracles at Agrigentum . . .	" 15.04
Temple "D" on the Acropolis of Selinus .	" 17.00
Temple of Athene at Ægina . . . . .	" 21.18
Temple of Artemis at Ortygia . . . . .	" 23.83
Temple of Theseus at Athens . . . . .	" 25.17
The Parthenon at Athens . . . . .	" 26.43
Temple of Nemesis at Rhamnus . . . . .	" 29.44

The average of twenty-one examples is 1 in 20.45.

The rates of diminution at Benihassan are plainly unconnected with this series. They are, approximately:—

Porch of Tomb 2 (16-sided) . . . . .	1 in 42
" " 1 (8-sided) . . . . .	" 55
Interior of Tomb 1 (16-sided) . . . . .	" 100

The ratio between the lower diameters of the shafts at Benihassan and their heights corresponds with that exhibited, not by the older Greek columns, but by those of the culminating epoch of Hellenic architecture. Mr. Fergusson seems to be at fault on this point. In the positive belief that the Greek but imitates the Egyptian order, he selects three examples to typify what he terms the three stages in the development of the Doric style,—the immature or imitative, the mature or perfected, and the degenerate stages. His first example—from the ancient temple of Corinth—"is one of the most massive specimens of architecture existing, more so than even its rock-cut prototype at Benihassan, from which it is most indubitably copied";\* the second is from the Parthenon, and represents the same order as it was refined and perfected by the sensitive Greek taste; while the third is "the weak and lean form of the Roman order of the same name."† His table of ratios—whence derived, I do not know—is as follows:—

\* Hist. of Architecture, i. 220.

† Ibid., i. 227.

Early, from Corinth . . . . .	1:4.47
Perfected, from the Parthenon . . . . .	1:6.025
Degenerate, from the island of Delos . . . . .	1:7.015*

To bring out the facts in the matter, I select from Dr. Krell's list a few instances, as follows:—

Temple of Athene at Ortygia . . . . .	1:4.27
Temple of Poseidon at Pæstum . . . . .	1:4.29
Temple of Artemis at Ortygia . . . . .	1:4.29
Temple at Corinth . . . . .	1:4.32
Temple at Assos . . . . .	1:4.47
Temple "D" on the Acropolis of Selinus . . . . .	1:4.50
Temple of Zeus at Selinus . . . . .	1:4.60
Temple of Concordia at Agrigentum . . . . .	1:4.67
Temple at Segesta . . . . .	1:4.82
Temple of Juno Lacinia at Agrigentum . . . . .	1:4.97
Temple "S" on eastern plateau at Selinus . . . . .	1:5.01
Temple of Apollo Epicurus at Bassæ . . . . .	1:5.13
Temple of Athene at Ægina . . . . .	1:5.30
The Parthenon at Athens . . . . .	1:5.47
Temple of Theseus at Athens . . . . .	1:5.62
The Fountain-chapel at Cadacchio . . . . .	1:5.63

The average ratio of twenty-five examples is 1:4.85.

The ratios of the Egyptian forms are, according to Lepsius:—

16-sided shafts, interior of Tomb 1 . . . . .	1:5.15
“ “ porch of Tomb 2 . . . . .	1:5.34
8-sided shafts, porch of Tomb 1 . . . . .	1:5.41

Mr. Fergusson, however, holds that "the Doric order, when first introduced from Egypt, partook of even more than Egyptian solidity";† which, if not verbally meaningless, is at least, in the face of these lists, misleading. For it appears that the columns at Corinth and most of those extant in Magna Græcia are so much stouter than the piers at Benihassan that they are quite incomparable with the latter, while it remains for the thoroughly Hellenic temples of Ægina and Bassæ and for the perfect Parthenon to furnish proportions like those of their supposably more clumsy prototypes.

Though not of prime importance, it may be interesting to mention

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\* Hist. of Architecture, I. 228.

† Ibid., I. 227.

the difference in respect of number of flutes. At Benihassan this number is either eight or sixteen; in the Doric order, regularly, twenty.\* The notable point here is, of course, that shafts with eight or sixteen sides suitable for flutes are naturally evolved from square pillars by replacement of angles, while twenty-sided shafts are not easily reached by that process.

Turning now to divergences in the number of members, we notice at once that the Greek order invariably has several members which the Egyptian has not. All these peculiar characteristics in the former order bear testimony to the presence of the true column idea in the Greek mind, and recall the thoughts of the beholder from the distracting hollows and edges of the flutes to the primal notion of a simple round support. These members are the cuts or grooves, usually one or three in number, near the top of the shaft; the swelling echinus that indissolubly unites shaft and abacus; and the annulets that encircle the lower part of the echinus. No trace of groove, echinus, or annulet occurs at Benihassan. The unbroken prism of the shaft meets the simple abacus-like projection of the architrave without the intervention of even a rudimentary intermediate member.†

On the other hand, the Egyptian order has one accompaniment, plainly borrowed from true columnar construction, which at the same time is entirely un-Greek. This member is the broad, circular plinth, taken from the Bundle Order of columns.‡ Joined to these simple pillars, it is obviously conventional and artistically incongruous. In the rare instances where plinths appear with the Doric order, they

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\* Krell, *op. cit.*, Table of Dimensions, &c.

† It has been supposed by some that Doric echini have been discovered at Karnak (Fergusson, *Hist. of Arch.*, i. 220; Falkener, *Mus. Class. Antiqs.*, i. 87; Reber, *Gesch. d. Baukunst im Alterthum*, Leipzig, 1869, p. 153); but Schnaase remarks (*Gesch. d. bild. Künste*, i. 336), "Es ist kürzlich mehr als wahrscheinlich gemacht worden dass diese vermeintlichen *Kapitüle* von Karnak in Wirklichkeit nichts Anderes als *Basen* sind"; and Krell says (*Gesch. d. dor. Style*, p. 26), "Ein gewöhnlich in den Handbüchern abgezeichnetes, angeblich protodorisches Capitäl von Karnak, an dem eine Art von Echinus erschiene, ist eine willkürliche Composition Falkeners aus Basen- und Capitäl-Fragmenten, wie Bergau und Erbkam (*Arch. Anzeiger*, 1863, p. 115) nachgewiesen." See figures in Fergusson and Reber as above, and Lepsius, i. 88. It may be added, that Sir J. G. Wilkinson makes a suggestion which may be properly called absurd about the derivation of the Doric echinus from the lower part of what he terms the "bud" capital. See his "Egypt in the Time of the Pharaohs," p. 156, and "Anc. Egyptians," ii. 298.

‡ See Essay II, § 4.

undoubtedly exhibit a totally different type from this. Ordinarily, however, the shaft rests immediately upon the stylobate, which is evidently considered competent to perform the function of plinth to the entire colonnade.

### § 7. *Internal Differences.*

But those differences between the true and "proto-Doric" which I have called *internal*, justify us in making still more radical distinctions. If we bear in mind the principles of criticism laid down in the opening pages of this essay, if we admit the total theoretical dissimilarity between columns and piers there insisted upon, and if we compare the forms before us with reference to this point with the scores of previous and contemporary architectural remnants that time has spared us in both countries, I think no one, after fairly canvassing the evidence, can doubt that different architectural ideas find embodiment in the two orders, in respect both of the fundamental character of the shaft itself, and of its relations to the adjacent members of the building. The inference is then easy, that the comparatively mature forms before us have descended from utterly diverse progenitors, and — unless we imagine a direct and avowed copying of these particular tombs at Benihasan by the architect of every early Greek temple, which is absurd — that the derivation of the Greek order from the Egyptian at any previous moment of their development is in the highest degree improbable, and becomes more and more inconceivable the further back we proceed.

The column, based on the tree type, rarely occurs (if at all) in Egyptian buildings of an earlier time than the XXXIII<sup>d</sup> Dynasty (305–80 B. C.); and when it does come in, it brings with it proofs of its derivation from the palm-tree in the proportions of its shaft and the decoration of its capital. Before this time, and particularly during the period when the Benihasan tombs were cut (XII<sup>th</sup> Dynasty, 2380–2167 B. C., according to Lepsius), the only supports of vegetable origin that we know anything about are plainly fashioned after water-plants, but never after cylindrical, log-like props.\* But the variety of primitive stone forms in actual existence to-day, and dating from the earliest known periods of Egyptian history (at least from Dynasty

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\* Almost the oldest Egyptian columns known are the few found at the southern tombs at Benihasan. They are beautiful reproductions in stone of a knot of four lotus-buds tied up with a string. See Lepsius, i. 60, and Essay II, § 4.

III., 3338–3124 B. C., according to Lepsius), is enormous. A graded list of known pier forms can be made out without difficulty, that shall include nearly every important theoretical variety of this quarry-derived member. The outlines of such a list have been incidentally given in the first part of this essay.

At the same time, it must be freely admitted that these primitive buildings, especially in the first great period of the Egyptian empire, that of the Pyramid-builders, while offering many beautiful instances of the growth of the pier idea, usually bear curious marks of predilections on the part of their architects for the methods and materials of the carpenter.\* In panel-work,† and in projecting eaves and rafters,‡ though not in upright supports, we are confronted by an unconscious reversion of forms to a different architectural type from that suggested by the material actually employed. The only adequate explanation of this fact seems to be that the Egyptian race migrated into Egypt from a much better timbered region, bringing with them the traditions of wooden construction; that after their arrival in the Nile valley they found stone so much more convenient, magnificent and durable that they adopted it for their public edifices; that the pier was first developed after the migration; that the earlier construction remained only in the impress it put upon the later; and hence that at Benihassan we have a marvellous, and, at first, perplexing conjunction of the two.

The Greeks, on the other hand, very rarely used the pier in the works of their best periods. Penetrate as far as we may into the history of Greek architecture, the column still appears as a frequent member.§ Both history and its own characteristics declare its derivation from wood. The historical references are well known and need not be rehearsed here,|| but the traces of wooden construction in the column itself are perhaps worthy of mention now: Besides the echinus, the astragal,—whether groove or moulding,—the plinth, and the projecting abacus, which are so difficult of explanation on any other supposition, the following characteristics add something to the

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\* Fergusson, i. 91, 99.

† Lepsius, i. 23, 24, 25, &c.

‡ Particularly at Benihassan. Mr. Fergusson allows that the panels in the tombs at Gizeh and elsewhere indicate a previous use of wood, but thinks that the construction of the Benihassan tombs points to the use of brick! (i. 99.)

§ Müller, *Anc. Art*, trans., p. 25. The word *κλειρ*, though not found in the *Iliad*, occurs twelve times in the *Odyssey*.

|| *Ibid.*, p. 25; Wilkins, *Athens*, p. 18.

plausibility of the wood-derivation theory. In the Ionic and Corinthian orders the flutes are parted by narrow, convex listels, the remnants of the rounded surface in which the flutes are imagined to be cut. In most of the examples of the older Doric style, the flutes meet in sharp edges, so that it seems hopeless to discover the basal form that the architect had in mind. In this discouraging situation, however, there is usually found a little three-cornered convexity between the tops of the flutes.\* If this three-cornered piece consisted of two planes meeting in a ridge which was continuous with the edge between the flutes below, the prism would be suggested as the original or fundamental form; but it is not so composed; it is a smooth convexity, a segment of the surface of a cylinder, so that, if a tranverse section of the column were made a centimeter below the echinus, it would be a circle, either unbroken or but slightly indented. Further, one of the temples at Pæstum shows columns whose flutes terminate a considerable distance below the echinus, leaving a wide zone at the top of the shaft to testify to the artist's idea.† Finally, a Doric column was found at Priene with regular listels such as the Ionic and Corinthian columns have.‡ The "proto-Doric" forms are without any such marks. No convexities anywhere intervene between the flutes; the angularity of the prism obtains from top to bottom. The flutes are sometimes omitted, leaving the prism unmodified,§ or, if they are present, at least one side is left unfluted for the reception of hieroglyphics.||

Again, the column and the pier bear different relations to the adjacent members, particularly the architrave and abacus. The pier recollects that in theory both it and the architrave belong to the same wall. Of this theoretical wall three reminiscences may remain: first, two short sections, attached to the side-walls, called pilasters; second, one or more central remnants, — perhaps somewhat modified, — whose length approximates to their thickness, which are the piers themselves; and, third, a strip from the top of the wall engaged with the roof, which may be called by analogy the architrave. The feature which betrays the affinity of these is the identical thickness of the architrave and of the bases, if not of the whole bodies of the pilasters and piers.

\* See, for example, the Dilettanti Society's "Ionian Antiquities," ii. 6, 18, &c.

† See Thomas Major, "Pæstum," plates 21 and 22.

‡ Ionian Antiquities, i. 18. Compare iii. 27 and 32.

§ No unquestioned example at Benihasan; but a good one from Karnak is photographed by Rougé, "Mission," plate 61.

|| Lepsius, i. 59; and Fig. 2.



The column, on the contrary, has no blood-relationship with the architrave. The two are brought together mechanically from different sources, and exercise only such influence over each other's dimensions as the most ordinary necessities of stability and congruity demand. The abacus, as already remarked, does not properly belong to the pier, although sometimes used with it. When so used, it is not as a development of the pier itself, but as the mere servitor of the architrave or an actual projection from it. When used with columns it ordinarily binds itself more closely to the capital than to the architrave.

This theorizing is justified by the differences between the true and false Doric orders. The former has a peculiar entablature (including the architrave) which always accompanies it; the latter has no such invariable accompaniment. And, even were the entablature equally invariable in the two styles, it is yet employed in different ways, the Doric being quite independent of the column and resting on but a portion of its top; the Egyptian imposing its thickness upon the shaft-base and resting on the entire shaft-top equally. Further, the abaci are quite dissimilar; the Greek projecting far beyond the lines of the shaft, and being united to it by a swelling echinus; the Egyptian being merely an outgrowth of the architrave. (Fig. 3.)

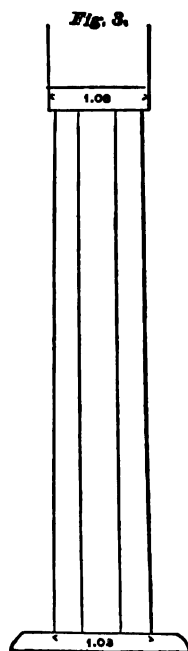
I may note, in closing, that all the differences and resemblances between the two orders are well exhibited in a comparison of the "Grottos" at Benihassan with the cave, to the eastward of Jerusalem, ordinarily known as the Tomb of St. James.\*

### § 8. *General Conclusion.*

This brings me to the end of my subject. If I have succeeded in showing by this rather extended piece of argumentation how the

\* Wilson, Jerusalem, photograph 39 b; Pierotti, Jerusalem Explored, plate 60.

FIG. 3. Side elevation of one of the octagonal piers in the portico of Tomb 1 at Benihassan. (From the measurements of Lepsius.)



Greek and Egyptian forms in question may have arrived at the similarity that they exhibit from entirely different starting-points; how it is probable, both from the general tendencies of architecture in the two countries and from the divergences of the forms themselves, that this difference of origin is real; and how this conclusion renders it altogether probable that the Greek order is *not* an imitation or derivative of the Egyptian, — I have attained my object.

## II. A CLASSIFICATION OF EGYPTIAN COLUMNS.

### § 1. *Introductory.*

IN the following essay I propose to present as complete a classification and description of Egyptian columns as the materials within my reach will permit. I was led to this line of investigation, and then to this formulation of results, by the difficulty I experienced in finding reliable digests of the phenomena of Egyptian architecture. Originally, then, I undertook this study simply to define and systemize my own knowledge. But subsequently I became convinced that several interesting conclusions about the early workings of the artistic instinct might be extracted from the accumulating treasuries of information which Lepsius, Champollion, and others have so carefully begun; and since such conclusions are necessarily conditioned upon a precise acquaintance with the actual forms, an additional motive was presented to continue the work already begun.

For a research of this nature two classes of material are at hand: first, hundreds of drawings and photographs collected by various royal and private expeditions into Egypt since the beginning of the present century; and, second, descriptions of the monuments in histories and books of travel. The assertions made in the sequel are almost entirely based upon the authority of plates and photographs. Of plates, the gigantic publications of the French and Prussian governments are much superior to all others. Of photographs, those taken by Rougé and by Dümichen are the best I have seen. To these is to be added a long list of books of variable merit and trustworthiness, each of which, however, more or less illumines some branch of the subject.\* On the

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\* The following list contains the most important: —

C. R. Lepsius: *Denkmäler aus Aegypten und Aethiopien*. 900 plates in 6 Abth. (12 vols.). Berlin, 1849–1878.

M. Jomard, edit.: *Description de l'Égypte*. 26 vols. of text; 925 plates in 12 vols. Paris, 1820–1880.

other hand, I have not dared to put much confidence in any statement unsupported by the testimony of the plates. So many flaws can be found in the accounts given by the various manuals of Egyptian history, antiquities, and art which I could consult, that I have become entirely distrustful of them all.

Yet there is nothing so recondite or difficult about the subject as to prevent its perfectly plain presentation. The statements of the following pages will all be of the most patent phenomena, so obvious that it seems truly marvellous that no succinct account of them is readily obtainable. It has been thought, indeed, that no clear separation of Egyptian columns into generic groups is possible, but this notion, as the sequel will show, is not wholly true, for in most cases the generic forms and the artistic conceptions on which they are based are quite evident.

I have ventured to add to the descriptions of the various columnar members a few notes on their mathematical proportions. These remarks take the position of notes because the generalizations of which they are the substance are drawn from too few examples to be in any sense final. They are trustworthy as far as they go, and are of some interest.

While I have considerable faith in the engravings from which the following descriptions are drawn, yet it is to be said that there is abundant opportunity for correction and emendation in them and in conclusions drawn from them. I only offer this study in the hope that it may serve as a convenient summary of the data at hand until something better appears.

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Johannes Dümichen: *Archäologische Expedition nach Aegypten. Photographische Resultate.* Berlin, 1871.

Le Vte. E. de Rougé: *Album Photographique de la Mission Remplie en Égypte.* Paris, 1864.

Champollion-le-Jeune: *Monuments de l'Égypte et de la Nubie.* 400 plates in 4 vols., with 2 vols. of descriptive text. Paris, 1835–1840.

Jules Gailhabaud: *Monuments Anciens et Modernes.* 4 vols. Paris, 1865.

Charles Lenormant: *Musée des Antiquités Égyptiennes.* Paris, 1835–1842.

Ippolito Rosellini: *I Monumenti dell' Egitto e della Nubia.* 9 vols. of text; 800 plates in 3 vols. Pisa, 1832–1844.

Vivant Denon: *Voyage dans la Basse et la Haute Égypte.* 1 vol. of plates, 1 of text. Paris, 1832.

To this list ought also to be appended, for greater completeness, the title of a new book which I have had no opportunity to see, — P. M. de la Faye: *Histoire de l'Art Égyptienne.* Paris, 1879. — For further titles, see *Catalogue of Books on Egypt and Egyptology, and on Assyria and Assyriology*, issued by Trübner & Co., London, 1880.

§ 2. *Sir Gardiner Wilkinson's Classification.*

The only formal classification of Egyptian columns that I have seen is that given by Sir Gardiner Wilkinson, the author of "*The Manners and Customs of the Ancient Egyptians*" (revised edition, London, 1879). This classification first appeared in a small hand-book called "*The Egyptians in the Time of the Pharaohs*" (London, 1857, p. 153), and was subsequently incorporated in substance into the article on "Architecture" in the *Encyclopædia Britannica* (9th edition). In outline it is as follows:—

1. Square pillars, "derived from the quarry, . . . taken from the mass left to support the roof of rock."

2. Polygonal pillars, formed from the preceding "by cutting off the four angles." Fluted pillars are included under this head; for it is added, "The next step was to hollow out the faces into grooves, and the only trace of the original column was then the central facette, which was left flat in order to receive a line of hieroglyphics."

3. Columns with "bud capitals," divided into three sub-genera according as only four or many plants are represented as tied together, or, all representation of separate stalks being omitted, the general shape only of the cluster is given. This group also, like the second, is regarded as a derivation from the first: "Pillars had always been painted with various devices, among which plants were the most common; these were afterwards sculptured in relief; and at length, when convenience required the angles to be removed, the pillar was cut away into the form of the plants hitherto sculptured upon its four sides; and the four plants alone being left, were represented bound together to account for their position and to complete the illusion."

4. Columns with bell-shaped capitals, "representing the same plant in blossom that the third order represented in bud."

5. Palm-tree columns, which copy from the preceding groups the cord wound about the upper part of the shaft as well as the cutting-in of the base of the same.

6. Columns with Isis-heads for capitals. These, too, result from the decoration of square pillars.

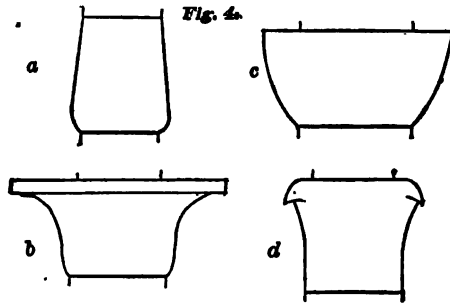
7. Composite columns, originating in the adornment of bell capitals, and the addition of some lotus forms. "In this order," too, "may be classed the volute-headed column, which was of great antiquity, at least as early as the beginning of the XVIIIth Dynasty, and which was derived from the water-plant typical of Upper, as the papyrus was of Lower Egypt."

8. Osiride columns, — square pillars with a figure of Osiris or of Typhon on one face.

This classification, besides being entirely unaccompanied by explanatory references and containing several assertions that are very difficult to verify, seems to betray considerable uncertainty in the author's mind about the primitive types of his several groups. At first he appears to derive Nos. 2, 3, 6, and 8 from 1; 4, in turn, from 3, and 7 from 4; so that all, with the exception of No. 5 (palm-tree columns), are traced back in the ultimate analysis to the quarry-pillar. Yet no sooner has he affirmed that the clay and reed hut borrowed the pillar from the quarry, than he adds, "But here the obligation ceased; and the built temple soon amply repaid the obligation by giving back to excavated monuments the water-plant, palm-tree, and other columns, with the architrave, plinth, abacus, and other members that could only originate in constructed work," — which is quite a different statement of the case. The former of these conflicting opinions seems, on the whole, to be the one to which Sir Gardiner really inclines. It has some features to which I cannot agree, and against which I shall present a few arguments further on. For the present it will suffice to suggest what I conceive to be a preferable scheme.

### § 3. *A New Classification proposed.*

For the sake of convenience and clearness, the form of the capital (see accompanying cut) is made the basis of classification, although



other members would in many cases prove equally decisive and serviceable. On that basis I should throw all the genuine columnar forms of Egyptian architecture into five groups, as follows: —

FIG. 4. Characteristic outlines of capitals of the first four Orders, in vertical section: — *a*. Order I. Bundle Columns; *b*. Order II. Papyrus Columns; *c*. Order III. Lotus Columns; *d*. Order IV. Palm Columns. (From various well-authenticated engravings.)

I. Columns with bulging capitals, — capitals which swell suddenly just above their base and then gradually taper upwards to the abacus. These columns invariably represent with greater or less distinctness a fascicle of water-plants. Hence we shall term this the Bundle Order.\*

II. Columns with bell-shaped or crater-form capitals, — capitals which rise in a compound curve, first convex, then concave, to a sharp, flaring edge. These columns seem to symbolize single plants. They constitute the Papyrus Order.

III. Columns with hemispherical capitals, — capitals which expand from below in a simple convex curve to an abrupt termination at the top. This we shall call the Lotus Order.

IV. Columns with capitals apparently formed of palm-leaves. This is the Palm Order.

V. Columns with human heads instead of capitals. As these columns usually bear the head of the goddess Hathor or Isis, they may be known as the Isis Order.

In comparing this scheme with Wilkinson's, it will be observed that groups 1, 2, 8, and part of 6 (supposing that it includes square and polygonal shafts decorated with Isis-heads) are not included here. These are laid aside to constitute a separate group, — Piers, simple, modified, or decorated,† — which I shall not attempt to discuss. Groups 3 and 5 are so obviously natural that they are retained as Orders I. and IV. Similarly, 4 and part of 7 are combined into Order II., — Papyrus Columns, capitals simple, modified, or decorated. The remainders of 6 and 7 then become Orders V. and III. respectively.

That the proposed classification is of practical utility I am convinced from a somewhat extended use of it in studying Egyptian architecture. That it is simple and natural is obvious; the types successively recognized being the stalk-bundle, the papyrus, the lotus, the palm, and the symbolic shaft with the head of a divinity. That it is comprehensive will appear, I hope, from an examination of the extant remains.‡

\* I have ventured to employ the word "Order" in this essay, not in the technical sense given it in Greek and Roman architecture, but in the sense in which it is used in natural history. See definition of the word in Penrose, "Principles of Athenian Architecture," (London, 1851,) p. 96.

† This exclusion is based on the theory advanced in Essay I., that the distinction between columns and piers should be insisted on.

‡ I have noticed but one irreconcilable form. This is described in § 5.

§ 4. *Order I. — Bundle Columns.*

Under this order I have classed all columns in which a bunch of water-plants, *without* open flowers, is directly or indirectly represented. This is probably the oldest,\* and on the whole the most characteristic variety of Egyptian columns. So fully does it typify the architectural genius of the nation that Ruskin (and others) may perhaps be pardoned the sweeping reference to Egyptian columns in general as "the gathered strength of river reeds."† The derivation of the order and its significance as an æsthetic product will be reverted to after some description has been given of its members, varieties, and decorations.

*Shaft.* — We shall begin with the shaft, because the varieties of structure which it exhibits afford the best basis for further classification. Three such varieties appear on the most casual examination, distinguished from each other by the different representation of stalks on the body of the shaft. In some cases only four stalks are delineated, in some, eight; while in others the number of stalks is not distinctly affirmed, but the general outline and many of the characteristics of the eight-stalk variety are so plainly employed that it is impossible not to regard this third variety as a modification or relative of the second. If these differences are made the basis of division, our classification may be thus extended:—

## Order I. — Bundle Columns.

(a.) Four stalks in shaft.

(b.) Eight stalks in shaft, stalks defined.

(c.) Eight (?) stalks in shaft, stalks undefined. (See cuts.)

- ▼ Adopting this scheme provisionally, let us pause a moment to examine the bottom of the shaft.

The lower part of the shaft displays two kinds of formation. Either, as in (a), the stems that compose it are cut off abruptly so as to rest squarely on the plinth; or, as in (b) and (c), the base is much contracted, as if the constituent plants are conceived to be springing from the plinth in a dense cluster. The first form gives the impression of greater stability and of material architecturally well utilized; the second, of greater naturalness and of a more conscious artistic effort. When uncontracted, the base is also undecorated; but when contracted, it is enveloped in leaf-like sheaths which seem to grow out of

\* This statement rests on internal evidence. See the hypothesis offered at the end of this section to account for the origin of the order.

† Stones of Venice, vol. i. ch. 8.

the plinth with the stalks. These leafy coverings are obviously reproductions of the bracts or sheaths which accompany reedy growths; and so, besides enlivening an otherwise barren surface, they enhance the impression of vitality which the general figure of the column has already produced. This decoration consists either of a single row of eight contiguous leaves (Fig. 7), or of two or three such rows, concentrically disposed, the points of the inner leaves falling in the intervals of the outer.\* The figure of the sheath is repeated in diminishing sizes within its outline, as though each sheath were composed of several decreasing layers.

Fig. 5.

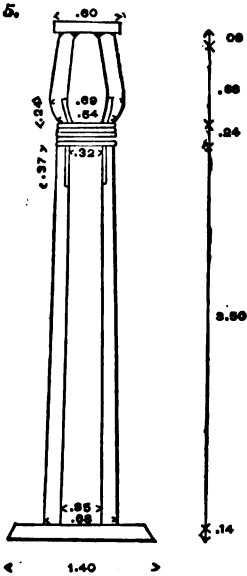
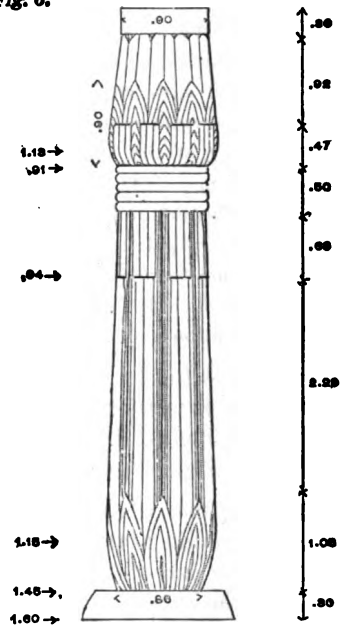


Fig. 6.



The main body of the shaft, as already stated, is either longitudinally incised in imitation of plant-stalks, or made to adopt simply the general shape of a bundle of plants without any distinction of stalks. In (a) the stalks are round; but in (b) angular (see cuts); and since

\* See Lepsius, i. 107, c.

FIG. 5. Bundle Column of the Lotus group, from Tomb 7 at Benihasan. (After Lepsius and Rosellini.)

FIG. 6. Bundle Column of the Papyrus group, first variety, from the Great Temple of Karnak. (After Lepsius.)



(c) follows (b) rather than (a) in most respects, we may conclude that theoretically it copies (b) in this particular also.\*

The apparent constituents of the shaft may be correctly said to be lilies and reeds. By lilies is meant *Nymphaeaceæ*, or "water-lilies" in the broad sense;† and by reeds, *Cyperaceæ*, or sedges.‡ These two families of plants, besides being somewhat widely separated in inter-

Fig. 7.

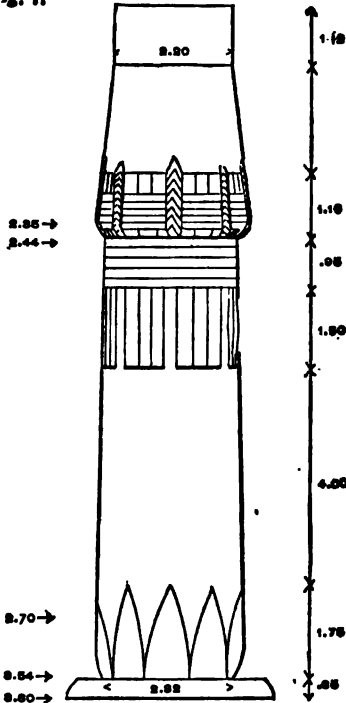
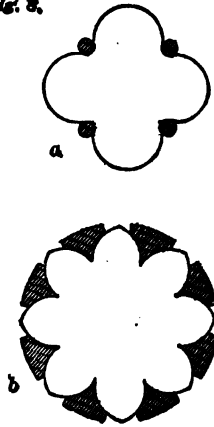


Fig. 8.



\* For a good specimen of sharp edges, see Rougé, plate 62. They have even been considered blemishes to the column: Long, *Fig. Antiquities in the Brit. Museum*, (London, 1846,) p. 113.

† See Gray, *Struct. and System. Botany*, (New York, 1873,) p. 385; *Manual*, (New York, 1858,) p. 22.

‡ Gray, *S. and S. Botany*, p. 496; *Manual*, p. 490.

FIG. 7. Bundle Column of the Papyrus group, second variety, from the Hypo-style Hall, Karnak. (After Lepsius.)

FIG. 8. Horizontal sections through capitals of the two sorts of Bundle Columns, showing difference of form both in the large stems constituting the shaft and capital, and in the astragal pieces that are inserted between the stems. (After Lepsius.)

nal structure, are also easily distinguishable in outward appearance. Among other characteristics, it is notable that the "lilies" have round, succulent stems,\* and the sedges angular, more or less siliceous stalks or culms.† Now, to these two families respectively belong the lotus ‡ and the papyrus,§ the most famous and in ancient times among the most abundant of Egyptian plants.¶ Various considerations, which will be noted in the proper place, combine to prove that the variety of bundle columns which we have called (a) is an imitation of four *lotus* stems, and the variety called (b) an imitation of eight *papyrus* stems. Among these considerations is the difference in form and decoration of the shaft-bases just described; for the lotus rises in distinct rope-like stems from a tuber deep under water and hence seldom visible, while the papyrus, like all sedges, springs from the mud in a dense clump of stalks surrounded by numerous sheaths.¶ Our provisional classification we will now expand into the following:—

Order I. — Bundle Columns.

A. Shaft composed of four lotus stems.

B. Shaft composed of papyrus stems.

1. Stems defined, eight in number.
2. Stems undefined.

\* See Gray, *Genera Floræ Americæ Boreali Orientalis Illustrata*, (Boston, 1848,) vol. i., plates 42 and 48.

† See, for good engravings of the papyrus-plant, John Hayter, *Report on the Herculanæum MSS.*, (London, 1811,) plate at end; and Segato, *Atlante Monumentale*, etc., ii. 59.

‡ *Nymphaea Lotus*, or *N. cœrulea*, or even *N. Nelumbo*, the Sacred Bean of India. See Wilkinson, *Anc. Egyptians*, ii. 407; the same, quoted in Rawlinson's *Herodotus*, (New York, 1859,) ii. 128; "*Archæologia*," (*Soc. of Antiquaries*, London,) xix. 276.

§ *Cyperus Papyrus*. For common uses, perhaps, *C. dives*, or even other sedges. Wilkinson, *Anc. Egyptians*, ii. 406; Rawlinson's *Herodotus*, ii. 129; Hayter, *Herculanæum MSS.*

¶ Kenrick (*Ancient Egypt*, i. 89), says: "The papyrus was found chiefly in the shallow waters of Lower Egypt, and hence became in hieroglyphics the emblem of that district; . . . the lotus, abounding more in Upper Egypt, was employed to denote that kingdom." He adds, that *N. Lotus* and *N. cœrulea* still grow in Egypt; but that *N. Nelumbo* has not been found. Wilkinson, however, affirms that neither the lotus nor the papyrus is properly included in the present flora of Egypt, the former occurring sometimes in the Delta, but not in the Nile itself, and the latter growing only in the Anapus, near Syracuse. Cf. *Isaiah*, xix. 6, 7.

¶ There is an exasperating misconception everywhere afloat in hand-books of Egyptian antiquities that the *lotus* has sheaths which are imitated on these columns. See, for example, Long, *Eg. Antiqs. in the Brit. Mus.*, p. 102; T. D. Fosbroke, *Encycl. of Antiquities*, (London, 1848,) i. 14.

As far as I have observed, the height of the shaft compared with the total height of the column (including plinth and abacus) is greater in A. than in B., — .78 in the former, from .61 to .70 in the latter.

A more decided difference between the two groups—one quite justified by the proportions of the natural types—is found in measuring the height of the shaft by its *greatest* (not lower) diameter. In A., the shaft-height is about 5.60 diameters; in B., never more than 3.96, and seldom more than 3.40.

No general statement can be made about the diminution of the shaft; for, although A. and B. 1 are strongly distinguished,—the one giving the ratio 1 in 27, the other quite invariably 1 in 16,—B. 2 is utterly lawless in this respect, oscillating from 1 in 57 to 1 in 9. This shift from uniformity to the lack of it seems to signify that, although the difference in types between A. and B. was distinctly understood at first, when B. 2 was designed, only the outlines of B. 1 were remembered, while its mathematical properties were usually forgotten.

*Plinth.*—Before we proceed with the upper parts of the column, the plinth demands a few words. In its simplest, and indeed almost only form, it is a circular elevation of the floor, a frustum of a cone or hemisphere. Sometimes the lower edge is slightly under-cut, but so rarely that the succision may be considered a purely fanciful alteration, a sort of decoration.\* Hence it will be enough to suggest the probable significance of the simple form.

If we bear in mind that these columns represent bundles of plants, may we not surmise that this wide basis, so totally unlike the Greek plinth, is a conventional symbol for the artificially modified mass of clay in which the stalks are conceived to be standing? May it not be that the Egyptian artist in imagination—as nurserymen not infrequently do in practice—reduced the earth around the plants to which he wished to call attention to a smooth surface, leaving immediately about the stems, however, a circular platform to serve as a kind of pedestal? The applicability of this hypothesis is greatest in the case of the papyrus columns with their constricted shafts, by which both the difference in nature between shaft and plinth, and the unity between plinth and floor are unmistakably affirmed. The hypothesis, furthermore, seems to be fully confirmed by various bas-reliefs, where the earth in which actual plants are pictured as growing is symbolized by precisely such a rounded platform.† The plants are conventionalized after the genuine Egyptian fashion; why may not the ground be conventional also? At all events, this plinth was evidently felt to be of the nature of a pedestal quite separate from the shaft, and commissioned mainly to raise it into greater prominence and stronger individuality.

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\* Description, ii. 4; Schnaase, *Gesch. d. bild. Künste*, i. 331.

† Lepsius, i. 80,—two square pillars with three plants on each.

With respect to height, as compared with the height of the whole column there appear to be two varieties of plinths, — one about twice the height of the other. The lower variety ranges from .027 to .029 of the column-height; the higher from about .045 to .070, and even more. The plinths of the lotus columns belong to the lower variety.

The greatest diameter of the plinth in terms of the greatest diameter of the shaft in A. is 2.06; in B. 1, 1.21 to 1.39, and upwards; in B. 2, 1.41 to 1.48. In B., however, being contrasted with the small *lowest* diameter of the shaft, the plinth appears broader than it really is.

*Astragal.* — Returning now to the upper part of the column, we find that always in A. and B. 1, and usually in B. 2, there is wound about the top of the shaft a cord-like astragal. This, when present, is invariably divided into five transverse bands or twists, which are notably horizontal, and not spirally ascending, as they would be if merely imitative of an actual ligature. In the older columns, A. and B. 1, these twists are carefully separated and rounded so as to give a distinct notion of their office and significance; but in B. 2, either they are flush with the surface of the shaft, and are only indicated by lines (Fig. 7), or they are omitted altogether.\*

In the sub-group A. the astragal occupies only .06 of the shaft-height; in B., it varies from .09 to .12.

*Astragal Pieces.* — Under the astragal, and occupying the depressions between the stems of the shaft, pieces of cane or lily-stems are slipped, as if to render the bundle rounder and more solid at the point of cincture, so that the large stems shall not be flattened and distorted by the pressure of the bandage.† In A. these pieces are small and round; in B. 1, large, and trimmed to a triangular shape so as to fit the gaps between the stalks with considerable accuracy (see cuts); and in B. 2, of course, they are only indicated by shallow outlines, or are entirely omitted.‡ The pieces employed in B. are regularly divided by vertical lines into three parallel strips, as if composed of three pieces. These strips are often bound together by bands not unlike the astragal, — horizontal, and usually five in number.§ In these pieces the difference in material between A. and B. is again emphasized, for in each case the same kind of stem is used as in the body of the column. The little scraps of lotus-stem only half fulfil their mission. They seem like experiments out of which the more adequate form developed.

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\* Lepsius, i. 101.

§ Ibid., i. 117.

† See Wathen, *Arts, Antiqs., and Chron. of the Anc. Egs.*, p. 98.

‡ Lepsius, i. 101.

It is remarkable that in all cases these pieces are much longer than mere utility requires, and furthermore are decidedly longer below the astragal than above it. Both these facts throw light on the æsthetic operation of the Egyptian mind. The apparent utility of the pieces is pushed somewhat into the background by so modifying them that they shall assume the rôle of decorations. A mathematical beauty is at the same time attained by making their length, measured both ways from the joint between shaft and capital, approximately equal below to one fourth of the shaft, and above to one third of the capital.

*Capital.* — The capital of this order is not so important or complex as in either of the other orders. The crowning member of the column is as yet but slightly "specialized," as biologists would put it. This particular kind of capital has ordinarily been called the "bud capital,"\* but this term is appropriate only when applied to the lotus columns, or when loosely descriptive of the *tout ensemble* of the capital. It is always misleading when applied to the papyrus columns, whose capitals are never composed of buds; and, since the latter group is much more numerous than the former, the name must be considered on the whole quite objectionable.

In the lotus group the capital consists of four buds, which terminate the four stems of the shaft. Their swelling bases and tapering points combine to give the capital its peculiar shape. That there may be no ambiguity in the matter, each bud is painted to represent the white of the flower just bursting through the green case of the sepals.† (Fig. 5.)

In the first sub-group of the papyrus columns the capital consists of a simple continuation of the component stalks of the shaft, their triangular shape and sharp edges being as carefully marked as before.‡ The presence of these edges, and the repetition of the exact forms found in the shaft, utterly exclude any *bud* theory here. The principal difficulty with this form is in justifying the swelling which produces the capital. If the stalks of the shaft are conceived to continue above the astragal, their combined diameter should gradually and uninterruptedly diminish. This not being the case, we are driven to an explanation which, though not generally received, seems worthy of acceptance; namely, that the protuberance of the capital is conceived to

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\* Wilkinson, *Anc. Egs.*, ii. 298; Kenrick, *Anc. Eg.*, i. 254; Schnaase, *Gesch. d. bild. Künste*, i. 331; Müller, *Anc. Art*, p. 219.

† Lepsius, i. 60; Rosellini, ii. 2.

‡ Long, *Eg. Antiqu. in the Brit. Mus.*, p. 118; Rougé, plate 62.

result from the pressure of the architrave upon the pliant stems.\* This explanation would be complete if it also showed why the bulge is at the bottom of the capital rather than at its middle height. The latter form seems to have been seen to be ungraceful, and abandoned for one which should in some measure repeat the figure of the shaft. It is also not impossible that the analogy of the true bud capital may have influenced this form.

If the second sub-group of papyrus columns be not wrongly interpreted, the preceding theory should apply to it also. This it does, I think, with special success; for although this capital has been understood to represent a single bud, its form is really not at all like a bud, — the expansion is too low and too abrupt. The point of greatest breadth seems to have been determined after the analogy of B. 1.†

The only decorations vouchsafed either of these capitals are sheaths similar to those found at the foot of the shaft. These, of course, are confined to the papyrus columns, where they are almost invariable. They regularly enfold the projecting edges of the stems, and alternate with the astragal pieces, under which they are partially concealed. (See cuts.) Their use can hardly be traced to any natural type. It was probably suggested by the sheaths on the shaft.

The relation between the top of the capital and the abacus is different with the two kinds of columns. The thin plate which surmounts the lotus columns extends considerably beyond the top of the capital; but the heavy block of the papyrus columns, with one exception,‡ conforms exactly to the dimensions of the top of the capital.

The proportions of the capitals I was able to compare are altogether too diverse to admit of any general theory concerning them.

The height of the capital, measured by the shaft-height, is about .22 in A., and from .28 to .88 in B. The same, measured by the column-height, is .17 in A., and from .20 to .25 in B. Again, measured by its own greatest diameter, it is 1.20 in A., and from .92 to 1.23 in B.

The greatest diameter of the capital in A. almost exactly equals the greatest shaft-diameter, but in B. it varies from .90 to 1.13 times that diameter.

In about half the examples, the greatest and least diameters of the capital are nearly proportional with the corresponding diameters of the shaft. The remaining examples depart widely from this proportion.

\* Wathen, Arts, etc., pp. 96, 109.

† Taking good examples of the three varieties, I find that in A. this point is about one fourth of the capital-height from its base; in B. 1, one seventh; and in B. 2, one twelfth.

‡ From the Fayoum. Lepsius, i. 47.

*Abacus.* — In A., the abacus so much attaches itself to the architrave that its size is determined by the width of the latter, and not by the diameter of the top of the capital; but in B. the architrave and column have established enough of reciprocity to demand of the connecting member the dimensions of both. The abacus is always square. Hence its corners project beyond the upper part of the capital, even when its sides do not.

The height of the abacus is less in A. than in B. Measured by the column-height, it is about .019 in A., and from .046 to .094 in B. Measured by its own width, it is .15 in A., .50 in B.

A condensed recapitulation of the characteristics of groups A. and B. will not be out of place.

A. Type, a bunch of lotus-stems with buds. Plinth low and conical. Shaft slender, over five diameters, of four round stems, not cut in at base, and without sheaths. Astragal narrow, of five twists. Astragal pieces simple, small and round. Capital, of four buds, without sheaths, low, nearly equal in diameter to greatest shaft-diameter. Abacus, low and projecting.

B.\* Type, a bundle of papyrus-stems. Plinth variable in height, hemispherical. Shaft stout, not over three and a half or four diameters, of eight triangular stems or adopting their general outline, cut in at base, sheathed. Astragal as before, but wider. Astragal pieces compounded of three sections, large, triangular. Capital, a continuation of shaft-stems, bulging under superincumbent weight, high and sheathed. Abacus high, projecting only at corners.

In the foregoing paragraphs I have aimed to give only those features which seem to be constant enough to be called characteristic and normal. A few rare forms now deserve a word or two.

A curious hybrid of the two species of papyrus columns is found at Dgebel-Addeh (?), according to Rosellini (iii. 3). The drawing is so wretched that no details can be described with certainty. It is enough to say that the capital of the first species is combined with the smooth shaft of the second.

Not infrequently bands encircle the body of the shaft similar to those which constitute the astragal at its top.† From this circumstance arises the oft-recurring remark that these columns are hooped like a

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\* It is to be understood, of course, that this description applies with greater explicitness to the first species of papyrus columns than to the second.

† Good examples in the temple of Luxor. Description, iii. 7.

barrel.\* This method of preventing the bursting of the column under its burden is noticeable, because it confirms the theory (presently to be enunciated) of the source of this columnar form, and because it accords with the explanation just offered of the expansion of the capital. For since an incumbent weight, sufficient to break down and bend back upon themselves the weaker tops of the stalks, would tend to spread apart the stiffer parts below, the presence of these bands implies the existence of such a pressure. In many of these twice or thrice bound columns the number of constituent stalks is different in different sections of the shaft. This may result from a fancied insertion of smaller stems in the intervals of the larger, but is more probably an independent variation of the type.

Lepsius gives (i. 107) an engraving of one Ptolemaic column from Philæ, whose capital is composed of several lotus-buds; but it must be regarded merely as a capricious deviation from the antique type, which needs no extended description.

It only remains to trace as best we may the genesis of these forms from natural types.† The possibility of thus tracing back its members to their origin, is one of the peculiarities of Egyptian architecture. Its types are not buried, as are the Greek and those of all subsequent styles, under many successive layers of alteration and refinement, but lie close to the surface, ready to be uncovered by any investigator. The earliest and simplest architectural method is here clearly exemplified in the free use of natural and purely mechanical forms as stepping-stones to artistic products. Of this method this group of columns is an excellent representative.

Sir Gardiner Wilkinson, as already remarked, regards these bundle columns as resulting from the decoration of square pillars.‡ In refutation of this view, it may be urged that, while utterly insufficient to explain the papyrus forms, it is highly improbable for the lotus group to which it was intended especially to apply, for two reasons. In the first place, there are no satisfactory illustrations of the progress of development from the unadorned pier to the comely shafts with their slender stems and buds.§ On the one hand, we have piers in the

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\* E. g., Gwilt, *Dict. of Architecture*, p. 87.

† Type, as I have used the term, is a form, whether natural or mechanical, which occasions the conception of an architectural form hitherto unemployed.

‡ Eg. in *Time of Pharaohs*, p. 153.

§ This refers of course to the indications of a gradual development of conceptions. No one could justly claim that a full series of actual remains is necessary



greatest profusion, with here and there one partially adorned with paintings or bas-reliefs; \* and on the other, columns representing a quartette of buds, without a trace of any connection with square piers, or of any preparatory stage of development. In the second place, some features found in the perfected forms must at least have been added after the entire emancipation of the bunch from its supposed early union with the pier. Such characteristics are the astragal, the astragal pieces, and the general form of the whole as related to the remainder of the building. To bring out the latter point, a comparison may be made between the southern and northern tombs at Benihassan. The former contain our principal examples of lotus-bud columns; the latter, only the fluted prisms of which so much was said in Essay I. In both cases there are instances of pilasters projecting from the side-walls in line with the columns or piers, but mark the difference: with the latter, the width of the pilasters exactly equals the diameter of the bottom of the pier, and, indeed, the pilaster is carried over by the architrave, and its width directly conferred upon the abacus; while with the former, the width of the pilaster is 8 cm. less than the lower diameter of the shaft, 9 cm. less than the greatest diameter of the capital, and about as much *greater* than the top and bottom diameters of the capital. (Figs. 2 and 5.) As these two forms are probably of the same period, the conclusion is inevitable that the pier was properly conceived to be a remnant, somewhat altered, of the wall indicated by the pilasters and architrave, while at the same time the column was as properly conceived to be undetermined except in position by the pilasters, an importation from another style of building, and hence really exempt from any limitation of dimension that the pilasters could impose.† These facts combined, though not absolutely disproving Wilkinson's theory, seem to render it quite doubtful.

For my own part, until some adequate proof of another derivation is advanced, I think it more reasonable to consider this lotus group a free and altogether creditable invention of early Egyptian fancy, the origin or occasion of which was the abundance of lotus-flowers in

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for the substantiation of any theory. The point here is simply that there is no satisfactory evidence in the actual forms that the conceptions of the Egyptians took the route suggested by Wilkinson to reach the lotus-bud column.

\* As for example at Zauiet-el-Meitin (Lepsius, i. 57; Reber, *Kunstgesch.*, fig. 9, p. 14, etc.), which example proves only that plants were depicted in bas-reliefs. As it represents open lotus-flowers, it really adds nothing to the probability of Wilkinson's theory.

† Compare Essay I, § 7.

nature, and their constant use in religious services and in the diversions of social life.\*

With the papyrus columns the case is much clearer, for but one theory is possible for their origin.† They are undoubtedly derived from the bundles of canes which were used instead of wooden beams in all Egyptian buildings of the earliest times and in all domestic architecture throughout the duration of the Egyptian empire.‡ Confirmation of this theory of early construction, if confirmation be needed, may be sought in the *a priori* naturalness in such a country as Egypt, almost devoid of trees, but abounding in reedy growths, of such a method of building; in the existence of the same custom at the present day, not only in Egypt, but in Mesopotamia and India; in the references in ancient writers to the practice; and in the overwhelming testimony of the monuments. If this hypothesis of origin be accepted, it were easy to compare type and antitype, Nature and Art, and discover the particulars in which the latter modified the products of the former to adapt them to her purposes. But the differences are perfectly obvious.

In view of the fact that the two varieties of columns just described seem to have had quite distinct origins, it may be a matter of surprise that they are grouped together here. The reasons for the collocation are two, namely, that they much resemble each other in composition of shaft and in outline of capital, and that they seem to have acted and reacted on each other to such an extent that the second variety of papyrus columns is in a measure the derivative of both lotus and papyrus forms. If the type assumed as the basis for division be simply a *stalk-bundle*, the present classification is correct. If it be preferred to mark two distinct types — a bouquet of lotus-buds and a building-sheaf of reeds — this order separates into two. Which classification is chosen is largely a matter of taste; the present one is the more concise and convenient,§ the other perhaps more thoroughly philosophical.

I have allowed this description of Order I. to become quite minute,

\* The abundance and importance of the lotus in ancient times are proved by its incessant recurrence on the monuments.

† Even Wilkinson employs this explanation a few pages before the classification quoted in the second section of this essay. Eg. in *Time of Phars.*, p. 148. Compare Wilkins, Athens, p. 9.

‡ See Viollet-le-Duc, *Habitations of Man in all Ages*, (tr. by Benj. Bucknall, Boston, 1876,) p. 76; T. B. Saint-Hilaire, *Egypt and the Great Suez Canal*, (London, 1857,) p. 256.

§ The lotus columns are almost too few to form an order by themselves.

because this order is the plainest of all, the one for the study of which the most plentiful materials exist, and because much that has been said will apply with equal force to other orders, the descriptions of which can therefore be made so much the shorter.

§ 5. *Order II. — Papyrus Columns.*

Under Order II. were grouped all columns with bell-shaped or "crater-form"\* capitals, whether simple or compound. This order can be confounded with no other except Order III., but the simple test of outline which was suggested in § 3 will suffice, I think, to distinguish it from the latter at sight.†

The difficulty in handling the phenomena of this order lies in the fact that, starting from one and the same type, it seems to have undergone two distinct processes of development, which, since they took place at widely separated periods, and under very diverse circumstances, led up to almost inconsistent results. In the first period, during the existence of the Great Theban Empire (Dynasties XVII. to XX.), these columns exhibit a stern simplicity analogous to that shown by Order I.; but in the second period, the era of the Ptolemies (Dynasties XXXII. to XXXIV.), under the stimulus of foreign enterprise and foreign canons of taste, this severity disappeared under a luxuriance of ornament that seems at first utterly alien to the native tendencies of Egyptian art. But on closer examination it is found that this new artistic life, though evincing unprecedented activity, obstinately clung to old methods and aims in confining its choice of types for its decorations to the familiar and oft-employed products of the national vegetation.

It is a striking fact that the bundle column, which is so common in earlier building,‡ was almost entirely discarded by the Ptolemaic

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\* Schnaase, i. 331.

† Although many writers seem to imagine that there is little or no difference in form between lotus-flowers and papyrus-bells. See, e. g., Long, *Eg. Antiqs.*, p. 106, — "the most common form of the capital is that of the calyx of a plant, probably the lotus"; Wathen, *Arts, Antiqs.*, etc., p. 109; Kenrick, *Anc. Eg.*, i. 254, — "the capital is shaped like a bell with its mouth upwards, the reflexed edge being an imitation of the opened flower of the lotus, or of the head of the papyrus." The difference in outline was, however, recognized by the Egyptians themselves, in their pictorial representations of the flowers; compare Lepsius, i. 26, with Rougé, p. 116, 118.

‡ It repeatedly appears in juxtaposition with the bell columns, supporting lower parts of the same halls, as at Karnak and Luxor.

architects. Its form seems to have been too unpretending, too inapt for elaborate ornamentation, for their use. Their own awakened taste, or the influence of Greek architecture, already past the summit of its perfection,\* prompted them to select that expansive form of capital which afforded the widest play for the fancy and genius of the sculptor.

It is hardly practicable to attempt to arrange the columns of this order into sub-groups, for although their capitals, as will be shown, are easily divided into groups, the differences of the latter seem to have had little or no influence on the other members. The only genera, therefore, which will be recognized will be based on a rough chronological division.

*Plinth.* — Very little need be added here to what was said of the plinth in Order I., except that, while in early periods it is usually similar to the plinth of the bundle columns and is amenable to the same interpretation, in later times it begins to discard the bevelled edge it had at first, and ultimately becomes a cylindrical drum to raise the column from the floor.† It thereby asserts its own individuality, shakes off its symbolic union with the ground, and by assuming vertical outlines proceeds to subserve the increased lightness of the shaft.

The plinth here is smaller than in Order I., the diameter in terms of the greatest shaft-diameter being about 1.50 in the early, and from 1.15 to 1.25 in the late examples.

The height of the plinth is almost as variable as before, ranging from .028 to about .060 of the height of the whole column.

*Shaft.* — Without much doubt the shaft of these columns was originally shaped much like that of the second variety of papyrus columns in Order I., attaining its greatest diameter some little distance above the plinth;‡ but in later forms the base of the shaft is no longer cut in, but descends sheer to the plinth with the abruptness of a palm column.§ Whether cut in or straight, the foot of the shaft is decorated with sheaths of various form and collocation, as before described.

\* The period of foreign dominion, which I have called for convenience the Ptolemaic, began in 332 B. C.

† See *Déscription*, I. 6, *et scpe.*

‡ The most magnificent example of the typical form of this order is found in the great Hypostyle Hall at Karnak, and is figured in one of the accompanying cuts. The lowest diameter of this example is but .92 of the greatest, and the interval between the two is about .07 of the shaft-height. This set of columns, by the way, is the highest in Egypt, measuring 20.36 m. (66 ft. 9.6 in.) from floor to architrave.

§ Compare *Déscription*, I. 18, with the cut in the next section but one

With reference to the idea involved in the body of the shaft, it is easier to say what it is not than what it is. The shaft is obviously not understood to be composed of separate stalks, like the bundle columns. But whether a single round stalk is symbolized, or the superficial shape of a bundle (although without any trace whatsoever of a fascicular composition) is represented, or the round form is selected without definite intention, is, I think, very doubtful.

The height of the shaft, referred to that of the column, is surprisingly constant, varying between .72 and .77, — which approaches the corresponding proportions of the lotus columns of Order I.

The shaft-height, measured by its greatest diameter, falls in some rather doubtful examples to 3.52 and 3.65, but varies in better authenticated ones between 4.15 and 5.50. These figures will be seen to range much higher than the corresponding ones for the papyrus group of Order I., and to approach those of the lotus group.

The diminution of the shaft is very irregular. In general it is much less than before, and in later examples the shaft verges upon cylindricity.

*Astragal.* — The astragal here is nearly the same as in the group called B. 2 in Order I. It is either very superficially represented or altogether omitted. Its position on the shaft is not quite constant; in later forms it is often separated from the capital by an interval about equalling its own width.\*

The width of the astragal falls between .075 and .111 of the shaft-height.

There are no proper astragal pieces.

As was just remarked, there is often an interval between the astragal and the capital. In this interval there seems to be a reversion to the bundle idea, for it is usually occupied by vertical stalks, sharp-edged or rounded, but nearly always small and numerous.† Yet the reversion is more apparent than real, for from the facts that bundle columns are not produced at the same period, that the most typical of the early forms lack these stems, that the stems themselves are so small, and, finally, that their position is ordinarily determined by that of the ornaments of the capital, I am convinced that they must be regarded as appendages of the capital, bound upon the *outside* of the shaft by the astragal. But although essentially a part of the capital, since its practical effect is to prolong the shaft beyond the astragal, I

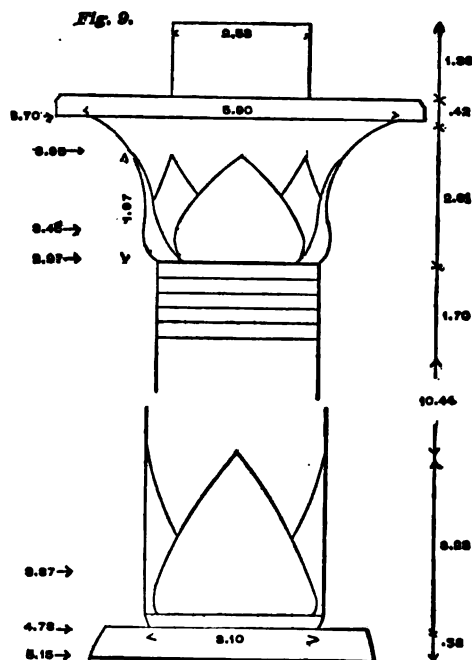
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\* Description, i. 8, figs. 6, 7, 9-15.

† Ibid., i. 8, fig. 12. In one instance a zone of triangular scales, similar to those presently to be described as belonging to the Palm Order, takes the place of these stems. See Ibid., i. 75, fig. 2.

have, for convenience in comparing different forms, reckoned this zone of stems when it occurs as part of the shaft.

*Capital.* — This clears the way for the description of the capital, which is by far the most interesting feature of this order. In the variety of its forms and decorations it is unique among the forms that come within the scope of this essay. In it the Egyptians displayed a fertility of invention which, though very late in their history, is national enough to afford considerable insight into their latent genius for artistic production which might have put forth its energies before and to better ends had not a tyranny of conventionality rigorously repressed and fettered it.



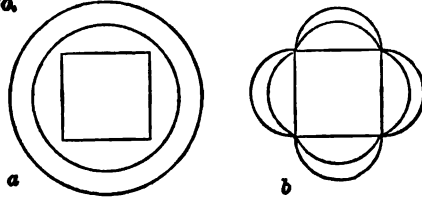
The fundamental form at the basis of this capital is precisely that of a very perfectly developed head of the true papyrus, and by common consent this coincidence is considered conclusive of its origin.

The simple bell is undoubtedly the primitive form, but compound

FIG. 9. Papyrus, or Bell Column, from the Hypostyle Hall, Karnak. (After Lepsius.)

forms are also found, mostly in later times, which, while preserving the peculiar vertical curves of the norm, seem to be produced by gathering four or eight half-bells round a common centre.\* Wilkinson, as we saw, threw these compound forms with all the lotus capitals into

Fig 10.



one promiscuous group, which he called "composite"; yet I think that after the difference between the lotus forms and these has once been recognized, the incongruity of that classification will be admitted. On the other hand, the similarity between the simple and compound bell capitals in basal shape appears to me sufficient to warrant their treatment together.

On the strength of these differences a sort of classification of the order may be attempted as follows :—

Order II. — Papyrus or Bell Columns.

A. With simple capitals.

B. With compound capitals.

1. Of four half-bells.

2. Of eight half-bells.

The noteworthy features about the shape of this capital are these. (Fig. 9.) At the bottom it leaves the shaft quite abruptly in a convex curve, so that there can be no doubt where the one begins and the other ends. Then, having attained a slight expansion, it rises nearly vertically until about two thirds of its height is reached, when it bends strongly outwards in a concave curve to the flaring edge peculiar to this order. The sweep of this concave curve is sometimes carried up so far that the edge of the capital seems to fall over. This edge is sometimes sharp, sometimes square. In either case it is joined by a bevel to the upper face of the capital. Normally this upper surface is perfectly flat,† but occasionally it is made to slope gradually up to the

\* *Déscription*, i. 21, figs. 1, 3, 4, 6. *Ibid.*, i. 75, figs. 4, 6, 10.

† See *Ibid.*, i. 7, fig. 1.

FIG. 10. Outline view of capitals of two groups of Bell Columns, taken from above, showing the important difference between simple and compound bells. (After Lepsius and the "*Déscription*.")

abacus.\* Mechanically regarded, this form of capital is extremely wasteful, the efficient portion of its expansion sometimes falling as low as .18.†

It would be a difficult task to describe and classify the manifold decorations which are applied to this capital. The subject could only be handled after more accurate data of the capitals were furnished, and an intimate acquaintance was had with the plant-life of Egypt. The subjoined list is therefore offered in the most tentative manner, in the hope that it may be revised by some competent hand.‡ I venture to distinguish eleven decorations, as follows: (a) Sheaths, like those at bottom of shaft; § (b) Square rings, as if one capital were set into another; || (c) Little bells on long sheaths, very similar to pictorial representations of papyrus-heads; ¶ (d) Long lanceolate leaves, straight or curved, with strongly-marked ribs; \*\* (e) Ovate leaves, divided palmately like fans; †† (f) Long, fern-like, pinnate leaves; ‡‡ (g) Short scraps of stem-like astragal-pieces; §§ (h) Projecting semi-circular brackets, reiterating in miniature the form of the whole capital; ||| (i) Embryonic volutes or scrolls; ¶¶ (j) Peculiar two-horned, calyx-like figures; \*\*\* (k) Even grape-vines.†††

A slight examination of these capitals suggests three remarks about the disposition of these decorations. First, they do not enter into the interior composition of the capital; indeed, they often seem to have stems which are slipped under the astragal. Second, as a rule they are evenly distributed around the entire circuit of the simple capitals, but grouped in and about the vertical hollows between the half-bells of the

\* Lepsius, i. 88, 89.

† In the great columns in the Hypostyle Hall, Karnak.

‡ It is said that there is a good classification of Ptolemaic capitals in the MS. department of the British Museum. See Wilkinson, *Anc. Egs.*, ii. 203, note 1.

§ Description, i. 8, fig. 15.

|| Ibid., i. 8, figs. 1, 2, 4.

¶ Lepsius, i. 81, a, b; 108, viii.

\*\* Description, i. 8, fig. 15. Compare leaflets of *Crucifera Thebaica*, *Déscr.*, (Natural Hist.), iii. 1.

†† Ibid., i. 75, figs. 1, 4, 6. Compare the same palm as under (d).

‡‡ Ibid., i. 8, fig. 14.

§§ Ibid., i. 56.

||| Ibid., i. 41.

¶¶ Ibid., i. 75, fig. 11; 78, fig. 5; Lepsius, i. 108.

\*\*\* Ibid., i. 75, fig. 9.

††† Ibid., i. 77, fig. 9.



compound ones.\* Third, however grouped, their height is so graduated that they practically divide the lower half of the capital into narrow horizontal zones.†

Although it is noticeable that the general form of the Corinthian capital is quite similar to this, yet the decorations of the two are almost entirely different. On the whole, it seems improbable to me that the latter was the derivative of the former.

The height of the capital, referred to the height of the shaft, varies from .15 to .25, with an average of .20 or .22; the same, referred to the height of the whole column, varies from .11 to .18, with an average of .15. Each of these ratios is less than in the papyrus columns of Order I.

The height of the capital in terms of its greatest diameter is .45 at Karnak (Hypostyle Hall), and in later times between .55 and .59. The ratio of height to breadth is here quite different from that in Order I; there it was about 1 : 1, here about 1 : 2.

The greatest diameter of the capital, measured by the greatest shaft-diameter, varies from 1.65 to 1.99 (Karnak). This is of course much greater than in Order I.

*Abacus.*—The abacus of all these columns is peculiar, because it touches so little of the top of the capital. It is merely an offshoot of the architrave, apparently commissioned mainly to keep the capital and architrave apart. Its usual form is cubical or nearly so, but in a few instances its height is very much exaggerated.‡ Its sides are often occupied by faces or even by whole figures. The subjects are either Isis-heads, such as compose the capitals of Order V,§ or figures of Typhon, the Egyptian spirit of evil.||

The height of the abacus, referred to the height of the column, is usually from .045 to .068; when extended, .18 to .26.

It may be interesting to call attention to an abnormal form of this order that is found in Tomb 81 at Gizeh, and is figured in the accompanying cut.¶ Its dimensions are so extraordinary that I venture to group them here by themselves. The plinth, if correctly given in Lepsius's plate, is rather high, — .043 of the column; very broad, — 2.14 shaft-diameters; and is strongly bevelled. The shaft is cylindrical, not cut in at the base; extraordinarily high, — .83 of the

\* Simple capitals, — Description, i. 8, figs. 14, 15; Lepsius, i. 81, a; an exception in Description, i. 42. Compound capitals, — Ibid., i. 8, figs. 6, 7, 9, 13.

† Ibid., i. 75, fig. 1. The same remark applies to Corinthian capitals.

‡ E. g., Ibid., i. 62.

§ E. g., Ibid., i. 21.

|| E. g., Ibid., i. 62, — the so-called Typhonium of Edfou.

¶ See Lepsius, i. 27; Reber, Gesch. d. Baukunst, fig. 91, p. 149.



columns are found in the covered hall — commonly called the Palace of Thothmes III. — in the extreme rear of the great temple-enclosure at Karnak.\* They are generally known as the columns “with reversed capitals,” although “with reversed shafts and capitals” would be more accurate.† (Fig. 12.) I had the curiosity to follow out this hint, and try the experiment of inverting the capital and shaft of one of these columns, (omitting, however, the section between astragal and capital,) and then comparing the proportions of the reconstructed column with those of ordinary bell columns. The capital proved to be a trifle too small for the top of the shaft, but the various proportions were strikingly accordant with previous results. The plinth is low, but not unprecedented, — .03 of the column-height; and of normal diameter, — 1.43 shaft-diameters. The shaft rises abruptly from the plinth, diminishes gradually, — 1 in 37; is rather heavy, — 3.60 diameters; but of excellent relative height, — .74 of the column. The capital-height, referred to the remainder of the column, is quite typical, — .20 of the shaft, .15 of the column; but is of unusually small width, — 1.14 shaft-diameters; making its height estimated by its own greatest diameter unusually great, — .64. Whether these curious coincidences touching the proportions of these columns really indicate anything concerning their origin I do not know.

Returning now to the normal form, the only necessary remark before passing on to the next order relates to the source from which the present order may be supposed to have been derived. The type is most obviously not mechanical, for no papyrus-bell was ever employed as an actual support; and at all events, whether the connection with the papyrus be accepted or not, such a capital combined with such an abacus is mechanically nonsensical. Hence I think we must again accord to the Egyptians the honor of selecting a natural form remarkable for its grace and importing it bodily into their architecture.

### § 6. *Order III. — Lotus Columns.*

Order III., comprising all columns with open lotus-flowers for capitals, differs little from Order II. except in this member. It seems to have been devised only to afford variety in the colonnades of the latter order, since it never occurs elsewhere, so far as we know, and there is

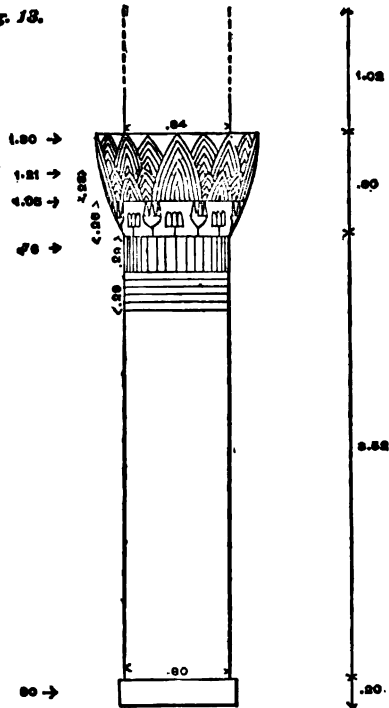
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\* See Lepsius, i. 81, *d*, *e*; *Description*, iii. 30; Reber, *Gesch. d. Baukunst*, fig. 97, p. 167.

† See Fergusson, *Hist. of Arch.*, i. 107; Wathen, *Arts, Antiqs.*, etc., p. 110; Murray's *Hand-book for Egypt*, (1873,) p. 442.

content meekly to accept the proportions in vogue among its associates. It will therefore be unnecessary to enter into any description of the lower parts of the column, except to say that they are like homologous parts in the later forms of Order II. Hence, since the upper and lower parts of the column cannot be regarded as wholly consistent, it must be confessed that this order is not altogether well distinguished, and, were it not for the utter difference in capitals, one would be tempted to combine it with the preceding.

Fig. 13.



*Capital.* — If we set aside the minor irregularities of its ornaments, which in truth only repeat the figure of the whole, the outline of the capital expands with considerable regularity and in one convex sweep from the shaft to a perfectly flat top. In the amount of convexity there appears to be a slight difference in the examples, most of them having the strong protuberance shown in the accompanying cut,

FIG. 13. Lotus Column, from Philæ. The abacus, bearing the head of Athor, with pylon above, is omitted. (After the "Description.")

while some have much straighter sides and slenderer figures.\* The capital consists of a great lotus-blossom, surrounded by buds, half-blossoms, and sepals, carefully colored in imitation of nature. The slight difference in degree of convexity just mentioned is made more important by the facts that the more frequent variety has more decoration and more complexity, while the rarer form is simply adorned by a row of sepals, and that the sepals in the former are quite flowing in outline, while those of the latter have square tips and nearly straight sides.† Very little decoration besides the sepals, etc., is employed. Certain obscure ornaments at the base of the sepals are not figured explicitly enough to be describable. As in the capitals of Order II., the ornaments are so disposed as to divide the capital into more or less regular horizontal zones. Furthermore, in evident imitation of that order, the expansion of the capital is rendered mechanically nugatory by the smallness of the abacus.

Since these columns always occur with bell columns, they are forced to adopt the same height of capital as measured by the column and shaft-height, namely, about .15 of the former, and .20 of the latter.

The capital-height, measured by its own greatest diameter, is a trifle greater than in Order II.,—from .59 to .62.

The greatest diameter of the capital is rather large,—about 1.90 shaft-diameters.

*Abacus.*—The abacus here does not essentially differ from that of Order II., either in form, dimensions, or decoration.

It is obvious that the statements already made in § 5, about the general character of the type employed and the general quality of the artistic effort put forth, are equally applicable here.

Before passing on to the next section, however, it is but fair to say that the examples of this order are so few that it is almost ridiculous to present generalizations of their characteristics. I have been able to learn of but *six* lotus columns, four at Philæ, two at Edfou.‡ They all belong to the Ptolemaic era.

#### § 7. Order IV.—*Palm Columns.*

The columns of Order IV. represent in shaft and capital the trunk and some of the leaves of a palm-tree. In many respects they are the most pleasing of Egyptian columns. Their general lightness and well-utilized energy contrast pleasantly with the cumbrous and irrational

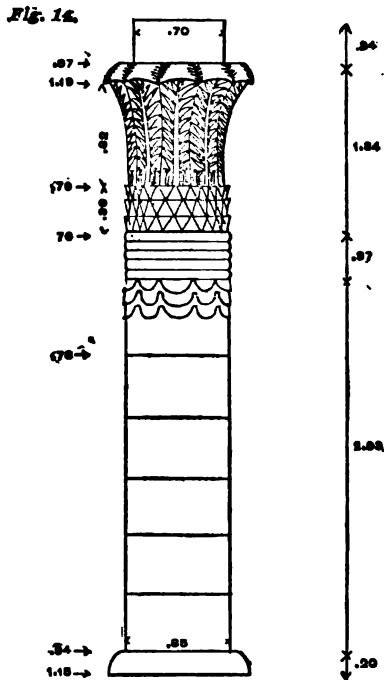
\* Compare Description, I. 21, fig. 8, with the same, fig. 2.

† Ibid., I. 21, fig. 2.

‡ Ibid., I. 6, 20, 21, 54; Lepsius, I. 108, i.

character of some of the forms we have already examined; and the type whence they are derived is somewhat more dignified and suitable to the important office of column than the water-plants hitherto selected.

These palm columns, like those of Order III., are frequently combined with representatives of Order II., and many features are possessed by the three orders in common. Indeed, in some cases it is much harder to discriminate the palm than the lotus columns from their numerous papyrus brethren; yet I think satisfactory distinguishing marks will be found when we come to the palm capitals.



*Plinth.* — The plinth does not differ materially from the later plinths of Order II. It is either partially or completely cylindrical, and does not depart widely from well-known proportions.

Its diameter ranges from about 1.15 to 1.60 shaft-diameters.

Its height varies from .035 to .050 of the column.

FIG. 14. Palm Column from Philæ, — now in the Berlin Museum. (After Lepsius.)

*Shaft.* — The shaft is eminently simple and plain. It is not cut in at the base, but is often decorated with the conventional sheaths. Just below the astragal peculiar semicircular festoons are sometimes found (see accompanying cut), which may be purely fanciful.

The height of the shaft, referred to that of the whole column, falls between .64 and .71.

The shaft-height in diameters varies from a very low example from Antæopolis (*Description*, iv. 41), 3.21, and several from about 3.90 to 4.31, to one remarkably high one in the environs of Eneh (*Ibid.*, I. 89), 5.10!

The diminution of the shaft is variable.

*Astragal.* — The conventional five-stranded astragal, although entirely unnecessary upon these solid shafts, is invariably present, and, curiously enough, is usually accompanied by a pendent loop, which points unmistakably to its origin in a cord or thong.\*

The width of the astragal is from .099 to .112 of the shaft-height, — a higher average than in Order II.

In one example, given in the above cut, there intervenes between the astragal and the capital a zone of triangular, upright scales, which at once suggests the zone of stalks that is so often found upon the later columns of Order II. Here, as before, the connection theoretically is with the capital, for the scales seem to symbolize the stiff sheaths which cover the origin of the fans whose graceful bending produces the capital. Perhaps the sculptor meant to imply that some of the lower and more scattered leaves had been stripped off, leaving the inner, fresher and more upright ones to form the crown of the shaft. Yet here again, in calculating the several proportions of the shaft and capital, I have chosen to combine this zone with the former, and for the reasons already given in § 5.

*Capital.* — At first sight it might seem that there is no good reason for regarding this group as aught but a strongly marked variety of Order II., but in fact the two groups are quite distinct. The differences between their capitals may be summarized as follows. First, the bell capitals are seldom, if ever, decorated with straight, narrow palm-fans; the palm capitals are always and only so decorated. Second, the number of the subdivisions of the former, when compound, is four or eight; of the latter, regularly nine.† Third, the subdivisions or half-bells of the former are horizontally convex, and separated by ver-

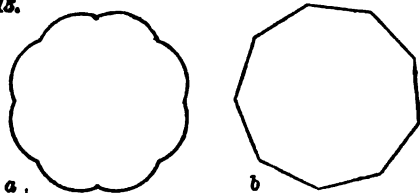
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\* See *Description*, iv. 41; Kenrick, *Anc. Eg.*, i. 255.

† Lepsius, i. 117, 119; *Description*, iv. 41; Kenrick, *Anc. Eg.*, i. 254.

tical grooves, so that a cross-section of the capital midway between top and bottom is a scalloped circle; the subdivisions of the latter are plane — except for the prominent midribs — or even slightly horizontally concave, and separated by sharp ridges, so that a cross-section similarly taken is a nonagon.\* (Fig. 15.) Fourth, the vertical section of the bell capitals is in the main concave, but begins at the bottom in

Fig. 15.



an unmistakable convexity; the vertical section of the palm capitals is continuously concave from the bottom to the drooping edge. (Fig. 4.) Fifth, the bell capitals are so much lower in proportion to their widths than the palm capitals that, when the two occur in the same colonnade, the latter equals the former *plus* the ring of stalks below it.†

The fans have a very pronounced midrib, from which the pinnately disposed leaflets project on both sides, unless, as sometimes happens, the detailed representation of the leaflets is omitted.‡ The tips of the fans droop considerably. At their bases there is sometimes an attempt to delineate a fruit-stalk.

The height of the capital varies from .27 to .32 of the shaft-height, and from .19 to .22 of the column. These figures rise much above those in Order II., and approach the highest in Order I., second group.

The height of the capital, measured by its own greatest diameter, is from .68 to .83, — again much above Order II., and approaching Order I., B.

The expansion of the capital ranges from 1.20 to 1.60 shaft-diameters, — which is less than in Order II., but greater than in Order I.

*Abacus.* — There is nothing of importance about the abacus except that its dimensions are by no means so ill-adapted to the supporting function of the capital as often heretofore. The architect's desire seems to have been to leave the tips of the fans unencumbered, and no more.

The abacus occupies from .037 to .066 of the whole column. It is not abnormally lengthened.

\* Lepsius, i. 119.

† E. g., *Déscription*, i. 6.‡ *Ibid.*, iv. 41.

FIG. 15. a. Horizontal section of compound bell capital with eight half bells.  
b. Do. of palm capital with nine fans. The difference between the two, not only in number of subdivisions but in their outline, is obvious. (After the "*Déscription*" and Lepsius.)



There is one example of this order, generally so consistent, whose proportions are so peculiar that they deserve special mention.\* The peculiarities are confined to the shaft and to the relations of other members to the shaft. The anomalous proportions are, shaft, .59 of column, 2.16 diameters; astragal, .132 of shaft; capital, .47 of shaft, .28 of column, but .71 of its own diameter; abacus, .095 of column. All these indicate that the shaft is considerably too short. Can the remains be wrongly reconstructed or measured?

There can be no question, I suppose, about the general type of this order. It is only necessary to note that this is the only Egyptian column incontrovertibly based on the *tree* type; that it borrows several incongruous features from other columns; that its figure is much stouter than that of its type, and indeed that the decided tendency to escape from strict subservience to natural types is evident in it throughout. Why the singular number *nine* should have been selected for the faces of the capital is not plain. Possibly it is to prevent the deeply incised elevation which an octagonal capital thus joined to a round shaft would present when regarded from certain points of view.

This order was principally employed in Ptolemaic times, but seems to have been invented somewhat earlier.

#### § 8. Order V. — *Isis-head Columns.*

Order V. comprises all columns with Isis-heads in place of capitals. This is an entirely unique form. Instead of a swelling top which appears to have some organic connection with the shaft, we have a group of four heads placed upon a round pillar.

As these columns are neither numerous nor important, I shall content myself with the description of a single example. I select for this purpose the most highly developed specimen of the order, — one of the twenty-four columns supporting the portico or front court of the great temple at Denderah.† (Fig. 16.)

*Plinth.* — It is evident that here the symbolic origin of the plinth is entirely forgotten. That member is employed and modified entirely without regard to any significance that it may once have had. It is circular and included within vertical sides, as often in Orders II., III., and IV.; but, unlike anything heretofore, is divided into three steps or layers, of which the third is the principal one.

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\* Lepsius, i. 119.

† A most magnificent engraving of one of these columns is given in *Description*, iv. 12.

The plinth is rather high, the three layers together occupying .059 of the column, the upper layer alone taking .042.

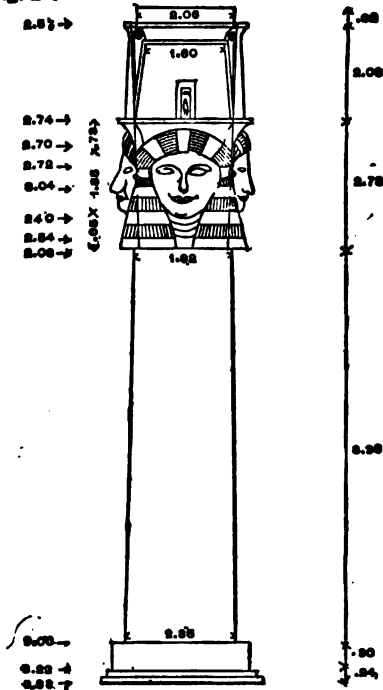
The diameter of the lowest layer is 1.44 shaft-diameters; of the upper layer, 1.30. These resemble the corresponding figures in Order II.

*Shaft.* — The shaft is perfectly simple, a tapering post unadorned by sheath, flute, or astragal.

Its height is unusually small, — .59 of the column, and 3.55 times its own diameter.

The rate of diminution is moderate, — 1 in 30.

Fig. 16.



*Capital.* — The free discussion of the peculiar and complex capital does not properly fall within the province of this essay. The most interesting part of the subject belongs to another department of study.

The head of Isis, with its accompaniments, is one of the common-places of Egyptian antiquities; it is constantly to be found on

FIG. 16. Athor-head Column, from the Great Temple of Denderah. (After the "Description.")

sistra, mirrors, vases, door-posts, abaci, and walls,\* an emblem of even greater frequency than the cross in modern times. And just as the true significance of the cross is to be determined by the student of religion rather than of art, so the significance of this emblem belongs to the history of religion rather than to the history of art. Hence I shall be content with a very cursory examination of it, laying all emphasis upon its characteristics as an architectural member.

The essential part of the capital is the sensuous, Oriental face of the goddess, with its double chin, elongated eyes and nose, voluptuous mouth, and unhuman ears. Around this is curved the conventional head-dress, wrapped by several ornamented bands and held in place by being passed behind the ears. Upon the head is placed first an ordinary Egyptian cornice, and upon this a pylon crowned with a second cornice. Through the door of the pylon is seen the asp so frequently recurrent in Egyptian ornamentation. On either side of the pylon is an upright, scroll-like member. All these features are conventional in the highest degree, as any one may convince himself by glancing through the engravings of Lepsius, Champollion, and Rosellini.

Touching the form of the capital as such, the following remarks suggest themselves. First, there is no connection between shaft and capital, but the latter is abruptly cut off at the bottom, as though the artist were unable to invent a satisfactory joint. Secondly, the capital falls into two quite distinct parts, the lower principal, the upper ornamental and accessory. Third, although, in consequence of the projection of the two side-faces, the capital appears on the whole wider at the bottom than at the top, yet in reality each separate face regarded from in front is considerably narrower below than above.

The effective width of the lower edge of the capital, i. e. looked at from directly in front of one of the faces, is 2.54 m.; of the widest part (at the point of the nose), 3.04 m.; of the first cornice, 2.74 m.; of the second, 2.57 m.; or, in terms of the greatest shaft-diameter, 1.08, 1.29, 1.17, and 1.08 respectively.

The width of each face or front taken by itself increases steadily from 1.92 m. (.82 diameters) at the bottom, and 2.06 m. (.88 diameters) at the first cornice, to 2.22 m. (.94 diameters) at the second.

The height of the whole capital is comparatively very great, — .57 of the shaft-height, .33 of the column. The two sections of the capital occupy .57 and .43 of its height, .33 and .24 of the shaft-height, .19 and .14 of the column.

The height of the whole capital, measured by its different widths, is, by the lowest, 1.87; by the greatest, 1.56; by that of the first cornice, 1.73.

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\* See Lepsius, i. 88, 100, 108; iii. 80, 82, 192; iv. 26, 40, 53; *Description*, i. 21; Champollion, i. 7; Rosellini, iii. 4; Wilkinson, *Anc. Egs.*, ii. 350, etc., etc.

The lower half divides into four horizontal sections: below chin, .65 m. high; face, 1.35 m.; head-dress above head, .51 m.; cornice above head-dress, .22 m. The face, therefore, occupies just one half the height of the lower part of the capital.

The greatest width of the face is between the tips of the ears, — 2.00 m. The width of the face proper at the same height is 1.43 m. The general form of the face is that of an equilateral triangle. Its vertical proportions are far from classic; being, lower face, .39, nose, .42, forehead, .19.

. *Abacus*. — The abacus is very low and well adjusted to the top of the capital.

Its height is only .022 of the column.

The genesis of this form is doubtful. Wilkinson of course connects it with the square pier, and in support of his opinion might have adduced many striking examples at various stages of development. Yet in the column under consideration there is absolutely no trace of such derivation. It looks more as if the four heads had been joined to a true columnar form. This speculation, however, is of little use, for this column belongs to so late and advanced a period that no perfectly distinct type can be insisted upon for it.

For convenience in comparison and reference, I subjoin a tabulation of the proportions I have noticed in the preceding pages.

	A.	I. B.		II.		III.	IV.	V.
		1.	2.	Early.	Late.			
PLINTH. Height, referred to column, Diameter, in greatest shaft- diameters,	.028 2.06	.045 — .070 1.21 — 1.89 +	2. 1.41 — 1.48	.028 — .060 1.50	1.15 — 1.25	.08 — .05 1.15 — 1.25	.085 — .060 1.15 — 1.60	.059 1.30, 1.44
SHAFT. Height, referred to column, " in greatest diameters, Diminution, — 1 in	.78 5.50 27	.61 — .70 3.40 — 3.95 15	9 — 57 (1)	.72 — .77 { 4.15 — 5.50 (reg.) } { 3.63 — 3.65 (?) } Less than in I.		.75 4.50 — 5.00 Vide II.	.64 — .71 { 3.90 — 4.31 } { 3.21, 5.10 (1) } Vide II.	.59 3.55 30
ASTRAGAL. Width, referred to shaft- height,	.06	.09 — .12		.075 — .111		Vide II.	.069 — .112	...
CAPITAL. Height, referred to column, " referred to shaft, " in greatest capital diameters, Diameter, (greatest,) in shaft-diameters,	.17 .22 1.20 1.00	.20 — .25 .28 — .38 .92 — 1.23 .90 — 1.13		.11 — .18 { .20 — .22 (reg.) } { .15 — .25 } .45	.55 — .59	.15 .20 .59 — .62 1.90	.19 — .22 .27 — .32 .68 — .83 1.20 — 1.60	.33 .57 1.56 1.29
ABACUS. Height, referred to column,	.019	.046 — .094		{ .045 — .068 (reg.) } { .18 — .26 (extended) }		Vide II.	.037 — .066	.022



## PROCEEDINGS.

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Seven hundred and twenty-second Meeting.

May 27, 1879. — ANNUAL MEETING.

The PRESIDENT in the chair.

In the absence of the Recording Secretary, Mr. Scudder was appointed Secretary.

The Corresponding Secretary read letters from the Microscopical Society of London, offering to the President of the Academy an election as Fellow of the Society; the Honorary Secretary of the Dominion of Canada, soliciting donations to the Public Library of Saint-John, New Brunswick, which had been destroyed by fire; and the Director of the École Polytechnique, offering an exchange of publications.

The Corresponding Secretary read the Report of the Council for the past year.

Mr. Lyman presented the annual report of the Treasurer and of the Auditing Committee.

Professor Lovering, on behalf of the Rumford Committee, proposed the following vote, which was passed: —

*Voted*, That the sum of three hundred and seventeen dollars and  $\frac{75}{100}$  (\$317.75) in the printer's bill for the past year be charged to the Rumford Fund.

Professor Cooke, on behalf of the Publishing Committee, stated that only about seven hundred and fifty dollars out of the one thousand dollars appropriated from the Academy's funds for printing had been expended during the past year; and, on his motion, it was

*Voted*, That the residue of the appropriation be applied to complete the forthcoming volume of Proceedings.

On the motion of Professor Cooke, it was also

*Voted*, To furnish authors of papers in the next volume of Proceedings one hundred copies of their memoirs, free of charge.

Mr. Scudder presented the annual report of the Librarian.

The following gentlemen were elected members of the Academy: —

William Lambert Richardson, of Boston, to be a Resident Fellow in Class II., Section 4.

James Craik Watson, of Ann Arbor, to be an Associate Fellow in Class I., Section 2.

Alpheus Spring Packard, Jr., of Providence, to be an Associate Fellow in Class II., Section 3.

The annual election resulted in the choice of the following officers: —

CHARLES F. ADAMS, *President*.

JOSEPH LOVERING, *Vice-President*.

JOSIAH P. COOKE, JR., *Corresponding Secretary*.

JOHN TROWBRIDGE, *Recording Secretary*.

THEODORE LYMAN, *Treasurer*.

SAMUEL H. SCUDDER, *Librarian*.

#### *Council.*

EDWARD C. PICKERING,  
JAMES M. PEIRCE,  
JOHN M. ORDWAY, } of Class I.

ASA GRAY,  
ALEXANDER AGASSIZ,  
HENRY W. WILLIAMS, } of Class II.

CHARLES E. NORTON,  
ROBERT C. WINTHROP,  
JAMES B. THAYER, } of Class III.



*Rumford Committee.*

WOLCOTT GIBBS,                   STEPHEN P. RUGGLES,  
 EDWARD C. PICKERING,       JOHN TROWBRIDGE,  
 JOHN M. ORDWAY,           JOSIAH P. COOKE, JR.,  
                                   JOSEPH LOVERING.

*Member of Finance Committee.*

THOMAS T. BOUVÉ.

The Treasurer, Corresponding Secretary, and Librarian were appointed a committee to consider the appropriations from the Academy's funds for the ensuing year.

On the motion of Professor Cooke, it was

*Voted*, To meet, on adjournment, at half-past seven o'clock, P. M., on June 11th.

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Seven hundred and twenty-third Meeting.

June 11, 1879. — ADJOURNED ANNUAL MEETING.

The PRESIDENT in the chair.

Professor Lovering presented the Report of the Rumford Committee.

Professor Lovering also presented the following votes of the Rumford Committee: —

*“Voted*, To recommend to the Academy to charge to the Rumford Fund the expenses incurred for the following journals during the years 1872–77, inclusive: Poggendorff's Annalen and Beiblätter; Comptes Rendus; Philosophical Magazine; Carl's Repertorium; Journal de Physique; Fortschritte der Physik; Dingler's Journal; Franklin Journal; Annales de Chimie; Quarterly Journal of Microscopical Science; and Philadelphia Photographer.”

*“Voted*, That, in consideration of the time of the Assistant Librarian spent in the service of the Rumford Committee between 1872–78, the committee recommend that the Treas-

urer be authorized to transfer five hundred dollars (\$500) to the general fund."

"*Voted*, That the list of periodicals contained in the records of the Rumford Committee, June 12, 1878, be paid for, including the binding, from June, 1878, to June, 1880, out of the Rumford Fund."

"*Voted*, That an appropriation of four hundred dollars (\$400) be made from the Rumford Fund for continuing the purchase of books upon light and heat."

These votes were severally confirmed by the Academy.

Professor Cooke presented the printed Report of the Council, and stated that the new volume of Proceedings would be ready during the present month.

Professor Peirce read the following papers: —

"On the Reference of the Unit of Length to the Wave-lengths of Light." By Charles S. Peirce.

"On the Meteoric Constitution of the Universe." By Benjamin Peirce.

Professor Pickering described the work now in progress at the Harvard College Observatory upon Nebulæ.

The following papers were presented by title: —

"The Temporary Change of Refrangibility in the Spectrum of Solar Protuberances." By Leopold Trouvelot.

"On the Supposed Existence of Two Permanent Zones of Solar Protuberances." By Leopold Trouvelot.

"On the Coefficient of Expansion of Nickel-plated Steel Bars." By William A. Rogers.

The following committees were appointed: —

*Committee on Publication.*

ALEX. AGASSIZ,      W. W. GOODWIN,      JOHN TROWBRIDGE.

*Committee on Library.*

EDWARD C. PICKERING,      HENRY P. BOWDITCH,  
WILLIAM R. NICHOLS.

*Auditing Committee.*

HENRY G. DENNY,      ROBERT W. HOOPER.

Seven hundred and twenty-fourth Meeting.

October 8, 1879. — STATED MEETING.

The PRESIDENT in the chair.

The following gentlemen were elected members of the Academy:—

Frank Austin Gooch, of Cambridge, to be a Resident Fellow in Class I., Section 3.

Nathaniel Dana Carlile Hodges, of Cambridge, to be a Resident Fellow in Class I., Section 3.

Edward Stickney Wood, of Cambridge, to be a Resident Fellow in Class I., Section 3.

Sir James Fitzjames Stephen, of London, to be a Foreign Honorary Member in Class III., Section 1.

Georg Curtius, of Leipsic, to be a Foreign Honorary Member in Class III., Section 2, in place of the late Friedrich Wilhelm Ritschl.

Professor Cooke announced that Professor Thayer would be unable to serve on the Council, and, on his motion, it was

*Voted*; To proceed to the election of a member of the Council to serve in place of Professor Thayer.

The result was the election of Mr. John C. Gray, Jr.

The President presented the names of the following gentlemen as members of the Centennial Committee:—

ROBERT C. WINTHROP, <i>Chairman</i> ,	
JOHN A. LOWELL,	H. H. HUNNEWELL,
ASA GRAY,	ERASTUS B. BIGELOW,
NATHANIEL THAYER,	J. INGERSOLL BOWDITCH,
WILLIAM B. ROGBBS,	JOSIAH P. COOKE, JR.,
B. E. COTTING,	ALEXANDER AGASSIZ,
ROBERT AMORY,	THEODORE LYMAN.

Professor Lovering presented a paper on Cosmical Physics, by Benjamin Peirce.

Mr. Sharples read a paper on the Constitution of Milk.

Seven hundred and twenty-fifth Meeting.

November 12, 1879. — MONTHLY MEETING.

The PRESIDENT in the chair.

The following papers were presented : —

“On the Relative Replaceability of the Bromine in the Three Brombenzylbromides.” By C. Loring Jackson.

“On a New Form of Astronomical Level.” By William A. Rogers.

“On Orthobrombenzyl Compounds.” By C. Loring Jackson.

“Measurements of the Satellites of Mars.” By Edward C. Pickering.

“On the Destruction of Insect Pests by Means of Diluted Yeast.” By Hermann A. Hagen.

The following paper was presented by title : —

“Motion and the Calculus.” By John Trowbridge.

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Seven hundred and twenty-sixth Meeting.

December 10, 1879. — MONTHLY MEETING.

The PRESIDENT in the chair.

The President read a notice of the late Erastus B. Bigelow.

On the motion of Professor Cooke, it was

*Voted*, That Mr. Edward Atkinson be appointed to fill the vacancy in the Centennial Committee occasioned by the death of Mr. Bigelow.

Professor Cooke read a letter from Professor G. Curtius, acknowledging his election as Foreign Honorary Member.

Professor Pickering spoke upon the desirability of the possession by the Rumford Committee of a standard measure of length and a standard kilogramme; an unusual opportunity for obtaining such a standard of length being now offered by M. Tresca, of the French Commission which has had in charge the determination of measures of length. Professor Pickering

presented the following vote on this subject from the Rumford Committee : —

*“ Voted, That the Academy be requested to appropriate a sum not exceeding five hundred dollars for the purpose of enabling the Rumford Committee to obtain, by direct comparison, accurate copies of the revised original standards of the French metre and kilogramme: these copies being considered indispensable for independent researches upon light and heat in this country.”*

The following papers were presented : —

*“ On the Magnetization and Demagnetization of Iron.”*  
By John Trowbridge.

*“ Apparatus for Illustrating Periodic Motion.”* By John Trowbridge.

Professor Trowbridge presented the following contributions from the Physical Laboratory of Harvard College : —

*“ Effect of Distance on Appreciation of Color.”* By W. H. Schwartz.

*“ On a Standard for Estimating the Reflection of Light.”*  
By A. H. Lea.

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**Seven hundred and twenty-seventh Meeting.**

**January 14, 1880. — STATED MEETING.**

The PRESIDENT in the chair.

Mr. Lyman presented a report of progress made by the Centennial Committee.

Professor Cooke called attention to the first part of Volume XV. of the Proceedings, just published. He also spoke of the plan of publishing a volume of memoirs to commemorate the one hundredth anniversary of the foundation of the Academy, and proposed that a note should be placed upon the notice of the next meeting requesting members who may have papers which could form a portion of the contemplated volume to notify the Recording Secretary.

Professor Charles R. Cross presented the following papers : —

*“ Photometric Researches.”* By William H. Pickering.

"Effect of Surface Condensation upon the Expansion of Gases." By Silas W. Holman.

Professor C. L. Jackson presented the following paper by title:—

"On the Relative Replaceability of the Bromine in Parachlorbenzylbromide, Parabrombenzylbromide, and Paraiodbenzylbromide."

On the motion of Professor Cooke, it was

*Voted*, That, when this meeting adjourn, it adjourn to the second Wednesday in February.

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Seven hundred and twenty-eighth Meeting.

February 11, 1880. — ADJOURNED STATED MEETING.

The PRESIDENT in the chair.

Professor Lovering called attention to the following vote of the Rumford Committee, presented at the meeting of the Academy on December 10, 1879:—

"*Voted*, That the Academy be requested to appropriate a sum not exceeding five hundred dollars for the purpose of enabling the Rumford Committee to obtain, by direct comparison, accurate copies of the revised original standards of the French metre and kilogramme: these copies being considered indispensable for independent researches upon light and heat in this country."

The appropriation was voted by the Academy.

The following gentlemen were elected members of the Academy:—

Josiah Willard Gibbs, of New Haven, to be an Associate Fellow in Class I., Section 2.

Clarence King, of Washington, to be an Associate Fellow in Class II., Section 1.

The following papers were presented:—

"The Relation of the Architect to the Underwriter." By Edward Atkinson.

"On the Mean Free Path of Molecules." By N. D. C. Hodges.

"On Taylor's Theorem." By John Trowbridge.

*Seven hundred and twenty-ninth Meeting.*

March 10, 1880. — STATED MEETING.

The PRESIDENT in the chair.

On the motion of Professor Cooke, it was

*Voted*, That, when the Academy adjourn, it adjourn to the second Wednesday in April.

The following papers were presented: —

“On Stellar Spectra.” By Edward C. Pickering.

“On the Atomic Weight of Antimony.” By Josiah P. Cooke, Jr.

Mr. Michelson described a plan for measuring the velocity of the solar system through space. Remarks upon this communication were made by Professors E. C. Pickering and W. A. Rogers.

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*Seven hundred and thirtieth Meeting.*

April 14, 1880. — ADJOURNED STATED MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read a letter from Professor J. Willard Gibbs, acknowledging his election as Associate Fellow of the Academy.

Professor Lovering presented the following vote of the Rumford Committee: —

“*Voted*, That the Academy be recommended to confer the Rumford Medal on Professor Josiah Willard Gibbs for researches in thermodynamics.”

Mr. Theodore Lyman spoke of the progress of the contributions to the centennial fund, and stated that the President's address would be delivered in the Old South Church, and that after the address a reception would be held at the hall of the Academy.

The following papers were presented: —

“On the Present State of the Question of Standards of Length.” By W. A. Rogers.

A standard metre from M. Tresca, of the French Commission, was exhibited.

"On a Method of obtaining a Permanent Record from Foucault's Pendulum." By Charles R. Cross.

"On Comets of Minimum Perihelion Distance." By Benjamin Peirce.

The following papers were read by title: —

"Substituted Benzaldehydes." By J. Fleming White.

"Dimethyluric Acid." By H. B. Hill and C. F. Mabery.

Professor Watson presented to the Academy the works of M. Cialdi on the movement of waves and littoral currents.

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**Seven hundred and thirty-first Meeting.**

**May 12, 1880. — MONTHLY MEETING.**

The VICE-PRESIDENT in the chair.

A letter was received from Mr. Clarence King, acknowledging his election as Associate Fellow; also, a letter from Dr. A. Schaffranck, announcing the establishment of the Natural History Society of West Virginia, at Wheeling.

Professor Alfred G. Greenhill, of Emmanuel College, Cambridge, England, at the request of Professor Lovering, spoke of the estimation with which Professor J. Willard Gibbs's work in thermodynamics is regarded in England, and said that the scientific opinion is that Professor Gibbs has advanced the subject more than any other man in late years.

Professor Greenhill presented to the Academy copies of several of his own papers.

Professor Pickering presented the following paper by title: —

"On a Mechanical Attachment for Equatorial Mountings to Facilitate Sweeping in Right Ascension." By D. P. Todd.

Professor Peirce read a paper on comets of minimum perihelion distance.

The following paper was presented by title: —

"The Columnar Architecture of the Egyptians." By Waldo S. Pratt.



## REPORT OF THE COUNCIL.

MAY 25, 1880.

SINCE the last Report, May 27, 1879, the Academy has received notice of the death of nine members, as follows: three Resident Fellows, William T. Andrews, Erastus B. Bigelow, and Thomas M. Brewer; four Associate Fellows, S. G. Arnold, H. C. Carey,\* Isaac Hays, and W. T. Roepper; two Foreign Honorary Members, J. C. Maxwell, and Viollet-le-Duc.

### RESIDENT FELLOWS.

#### WILLIAM TURELL ANDREWS.

WILLIAM TURELL ANDREWS, A.M., the son of Ebenezer Turell and Hermione (Weld) Andrews, was born in Boston, December 24, 1794, and died there November 24, 1879, aged eighty-four years and eleven months. He entered Harvard College in 1808, when only thirteen years old, and graduated in course with such well-known men as Peleg Sprague, Edward Brooks, and Dr. John Homans. After leaving college, he began the study of the law, and entered the profession, but soon relinquished the practice of it, if indeed he had entered upon it. He was fond of retirement and of study, and devoted much of his leisure to the reading of the classics. He likewise filled many offices of trust. From 1853 to 1857 he was Treasurer of Harvard College. It is said that the salary voted to him he gave to the Plummer Professorship. He was a trustee of the McLean Asylum and Massachusetts General Hospital; a trustee of the Boston Public Library; a member of the Massachusetts Charitable Fire Society; a director of the Massachusetts Mutual Insurance Company; a director of the City Bank, and its President for many years. He was for a long period connected with the Provident Institution for Savings, as Secretary, Trustee, and Vice-President. He was also for many years a

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\* Notice in the next Report.

trustee of the Boston Athenæum. He served for six years as representative to the Massachusetts Legislature. In 1851 his father died, bequeathing him a large estate. Mr. Andrews left a widow, two sons, and three daughters, the eldest of whom married the late Dr. John B. S. Jackson, of this city. Mr. Andrews was a man of much kindness of disposition and great elegance of manners. For two years before his death he was afflicted with paralysis in his legs. He was elected a member of this Academy, November 11, 1857.

#### ERASTUS BRIGHAM BIGELOW.

DURING the past year the Academy has lost one of its most valued members by the death of Erastus Brigham Bigelow.

He had a genius for mechanics; his name will be remembered as one of the great inventors of his time, and as one who had a rare faculty in the application of science to the useful arts.

He combined in a marked degree the qualifications of a sagacious man of business with those of a skilful mechanic, and thereby succeeded in accumulating an ample fortune, the income of which was wisely spent. It may well be said of him that the dollars of his wealth measured the services he had rendered.

Mr. Bigelow took an active interest in the discussion of the social and political questions of his time, and has left many valuable records that will be of service to students when the financial history of the last quarter of a century is written.

He treated questions of business and of taxation with marked ability, and it remains for time to prove whether he was as successful in solving the vexed questions in these branches of social science as he was in perfecting the complex machinery with which his name is identified.

#### THOMAS MAYO BREWER.

THOMAS MAYO BREWER was born in Boston, November 21, 1814, and died, after a short illness, at his residence in that city, January 23, 1880. He graduated at Harvard College in 1835, and from the Harvard Medical School in 1838. Entering immediately upon the practice of his profession, he held for some years the position of Dispensary Physician at the North End. On abandoning the profession of medicine, he became one of the editors of the Boston Atlas, and continued his connection with the paper till it was merged in the Boston Traveller, attaining considerable distinction as a political

writer of unusual ability. He soon after became a partner in the well-known publishing firm of Swan and Tileston, his connection with which (later under the names of Hickling, Swan, and Brewer, and Brewer and Tileston) continued till 1877, when he retired from business and passed two years in Europe.

Dr. Brewer early evinced a strong interest in ornithology. He was a warm friend of Audubon, whom he materially assisted in his great work on North American Birds. As early as 1837 he published a noteworthy paper on the birds of Massachusetts, and from this date until his death was a frequent contributor of articles relating to his favorite science to several of the scientific and literary journals of the day. Although confining his attention mainly to the department of oölogy, he became well known as an ornithologist, both in this country and abroad. His larger works embrace (1.) a popular edition of Wilson's "American Ornithology," published in 1840, to which he contributed a "Synopsis" of all the birds then known as North American; (2.) a work entitled "North American Oölogy," devoted to an account of the geographical distribution of the birds of North America during the breeding season, and embracing figures and descriptions of their eggs; and (3.), with Professor Spencer F. Baird and Mr. Robert Ridgway, he shared the authorship of "A History of North American Birds," to which he contributed the biographical portion. The "Oölogy," owing to the great cost of the illustrations, was not continued beyond the first part, embracing the Birds of Prey, the Swifts, Swallows, Goatsuckers, and Kingfishers, which was published in 1857, in Volume IX. of the "Smithsonian Contributions to Knowledge." He continued, however, to collect material for its completion, of which there was reasonable prospect of accomplishment. Three volumes of the "History of North American Birds," embracing the "Land Birds," appeared in 1874. At the time of his death Dr. Brewer had finished the final revision of the manuscript of his share of the remaining portion of the work. His collection of eggs, which by his will he left to the Museum of Comparative Zoölogy of Cambridge, was one of the largest private collections extant, embracing over three thousand species and not far from fifteen thousand specimens.

His interest in educational matters led to his election in 1844 to the Boston School Board, to which he was recently rechosen for the term of three years, and of which he was the senior member. Fidelity to friends and to his convictions of truth and duty were marked traits in his character, while socially he was greatly esteemed.

Dr. Brewer was a grandson of Colonel James Brewer, a patriot of

the Revolution and a leader of the "Boston Tea Party" of 1773. He was married in 1849 to Miss Sally R. Coffin, daughter of Mr. Stephen Coffin, of Damariscotta, Me., who with a daughter survives him.

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## ASSOCIATE FELLOWS.

## SAMUEL GREENE ARNOLD.

THE HON. SAMUEL GREENE ARNOLD, elected an Associate Fellow of the Academy Nov. 9, 1859, died on the 12th of February last, in his fifty-ninth year. Born at Providence, R. I., April 12, 1821, he was graduated at Brown University in 1841, and afterwards pursued his professional studies at the Cambridge Law School. He was more than once Lieutenant-Governor of Rhode Island, and for a brief period a Senator of the United States for that State. During the late civil war he served the Union cause for some time as a volunteer Aide-de-Camp to Governor Sprague. He was President of the Rhode Island Historical Society for many years, delivered many addresses, and contributed numerous articles to historical and literary periodicals. His principal work was a "History of Rhode Island," in two volumes, first published in 1859-60.

## ISAAC HAYS.

DR. ISAAC HAYS died at his residence in Philadelphia on the 12th of April, 1879, aged eighty-three years.

He was born in Philadelphia, and after taking his degree in Arts at the University of Pennsylvania, in 1815, he entered his father's counting-room, and was for a time engaged in the East India trade. But he soon found this uncongenial work, and, leaving the office, he again entered the University and took his degree in medicine in 1820.

In 1827 he was appointed on the editorial staff of the Philadelphia Journal of the Medical and Physical Sciences, which afterward became the American Journal of Medical Sciences, and for more than fifty years his best energies were devoted to editing this Journal, with an ability, judgment, and industry which placed it in the front rank of American medical publications, and gained for it an honored position abroad.

Finding that the profession were in need of some more frequent publication of the same high standard, he began a monthly supplement,

the *Medical News*, in 1843, and in 1874 the *Monthly Abstract of Medical Sciences* was started under his direction.

In 1834 he planned and published two volumes of the *American Cyclopædia of Practical Medicine and Surgery*, which was intended to be the most thorough and elaborate treatise of the time. He had as contributors such men as Bache, Chapman, John C. Warren, Dewees, and many other distinguished men. The parts which were published, and to which he himself contributed largely, showed the high character of the work, which only failed of success on account of the meagre support it received from the profession at large.

His first contributions to medical literature were two papers on *Purulent Ophthalmia*, and another on *Inflammation of the Sclera*.

In 1822 he was appointed one of the surgeons to the *Pennsylvania Infirmary for Diseases of the Eye and Ear*; and in 1834 he obtained a similar appointment to the *Wills Ophthalmic Hospital*, — a post which he filled and honored for twenty years.

In 1843 he edited, with valuable additions, a *Treatise on Diseases of the Eye*, by Sir Wm. Lawrence; and in other years *Arnott's Elements of Physics*, *Hoblyn's Dictionary of Medical Terms*, *Broussais's Chronic Phlegmasiæ* and his *Principles of Physiological Medicine*, were published under his careful supervision.

In 1828 he published an edition of *Wilson's American Ornithology*, and from the time when he was made a Member of the *Academy of Natural Sciences of Philadelphia*, two years before he took his medical degree, until his death, he always took a warm interest in natural history, and delighted to pass many hours in the study of his favorite subjects.

During a long life Dr. Hays devoted himself with rare energy and ability to raising the standard of medical literature in this country; as a continuous service of over half a century on the *American Journal of Medical Sciences* will show.

Dr. Hays was honored and loved in all his social relations; and will be missed, not only by those who knew him personally, but by the profession at large.

WILLIAM T. ROEPER.\*

PROFESSOR WILLIAM T. ROEPER of Bethlehem, Pennsylvania, died on the 11th of March, at the age of seventy. Professor Roep-

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\* From "The American Journal of Science."

per was born in the village of Peilau, near the Moravian settlement of Gnadenfrei, in Lower Silesia, Germany, March 7th, 1810. In early life he qualified himself for service in the Moravian Church, and for several years taught at different church schools. He came to America in 1840, at the request of the authorities, to engage in the financial work of the Moravian Church, and was employed in this until 1869, residing most of the time at Bethlehem. At the opening of the Lehigh University in 1866, Mr. Roepper was appointed Professor of Mineralogy and Geology, and Curator of the Museum. He retained the professor's chair only three years, discharging his duties with marked success during that time, but he remained Curator of the Museum until 1871. The latter years of his life were spent in the scientific and historical studies in which he was so much interested.

In the death of Professor Roepper the science of his adopted country has met with a real loss. Independent of his scientific attainments, he was a man of unusual culture, a thorough scholar in the classics and in history, and an accomplished musician. It was to mineralogy, however, that he especially devoted himself, and in this branch of science he occupied a high position. The mathematical relations of the forms of crystals was a subject to which he gave much study. He was not less diligent in the chemical investigation of minerals, and his thorough knowledge of the practical side of mineralogy caused his opinion as an expert to be frequently sought by those engaged in the mining and smelting of ores. The discovery by him of deposits of zinc ore in the Saucon Valley, Penn., was one which did much to benefit the town in which he resided, but from which he gained nothing himself. He contributed several papers on mineralogical subjects to this Journal; one of these deserves especial mention because a mineral species there described, an iron-manganese-zinc chrysolite from Stirling Hill, N. J., is now called *Roepperite* after him. Those who knew him well will appreciate that, as the result of his patient work, his contributions to scientific literature might have been much more numerous but for the delicate modesty and lack of desire for outside reputation which characterized him.

Professor Roepper was a man of most genial and attractive personal character, who will be long remembered by all who had the privilege of his intimate acquaintance.

## FOREIGN HONORARY MEMBERS.

## HEINRICH WILHELM DOVE.\*

HEINRICH WILHELM DOVE, who has been a foreign honorary member of this Academy since Nov. 14, 1859, was born in Liegnitz, Silesia, on the 6th of October, 1803, and died in Berlin on the 4th of April, 1879. He was the youngest child of a prosperous merchant who had been twice married. Of this large family, only two, own sisters of Heinrich, lived to an advanced age. While young Dove was still in his childhood, his father suffered serious reverses from the depression of business and the crushing taxes produced by the wars of Napoleon the First. His mother, left a widow in 1810, continued the business of his father, and made great exertions and sacrifices in order to give a good education to her children. Dove was diligent and successful in his studies, and at the age of twelve he was sent to the Ritter Academy. Here he so distinguished himself, especially in mathematics, as to be called by his companions the Little Professor. At the age of seventeen he was prepared for the University. Cradled in one of the stormiest periods of European history, Dove had passed his childhood and youth within sight or sound of stirring events, the memory of which never faded from his mind. The years 1813-15 particularly, and the retreat of Jahn after the battle of Katzbach, produced a profound impression upon him. In later life he indulged in reminiscences of his youth: telling the story of his being compelled to eat before the French grenadiers, because they were afraid of being poisoned.

At Easter of the year 1821, Dove entered the University of Breslau, where he passed six semesters, devoting himself at first to philological studies. But he soon came under the influence of Brandes, the Professor of Mathematics at Breslau from 1811 to 1826. His lectures on mathematics, astronomy, physics, and meteorology attracted many students by their substance and the happy manner of its presentation. When Dove entered the University, Brandes had just published his *Beiträge zur Witterungskunde*, and had recommended meteorological observations. While students at Göttingen, Brandes and Benzenberg had determined, by parallax, the distances

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\* The death of Dove, although reported last year, took place so near the time of the Annual Meeting that this notice was necessarily deferred until the present Report.

and velocities of shooting-stars and meteors; and had assigned them their true place in the Cosmos, outside the earth's atmosphere. Under this new inspiration, Dove abandoned his first love, and courted the natural sciences, especially physics and mathematics. But he was not destined to complete his studies at Breslau. Academical life at this time was full of excitement. In 1815 the national alliance of German students (*Burschenschaft*) was formed: the Wartburgfest of 1817 had given many an opportunity to join this association. Although it was forbidden in 1819, after the murder of Kotzebue, the fellowship continued. At the Jubilee of Dove's doctorate, in 1876, Dr. Falk said that his father and Dove were not only classmates (*Primaner*), but fellow-members of the *Burschenschaft*; and that, while his father had the taste of the inside of a fortress, Dove came off with exile.

Dove went to Berlin, to continue his studies. There he gave his time to physics, and was in intimate friendly relations with the eminent interpreter of that subject, Paul Erman. He also studied diligently Hegel's philosophy, including his natural philosophy; but he did not conceal the fact that he was not a convert to the Hegelian philosophy. He graduated on March 4, 1826, and in his dissertation for the Doctor's degree, *De Barometri Mutationibus*, he first blossomed out as a meteorologist, and foreshadowed the career in which he was to achieve his greatest distinction.

Dove was now twenty-two years old. The death of his mother had left him wholly to his own resources, since none of his brothers could aid him in the intellectual objects of his ambition. He left Berlin and took up his residence in Königsberg for the study and teaching of the physical sciences. At first he was a *Privat-docent*, and for two years Professor Extraordinary. In the first semester of 1826-27, he instructed publicly in thermics, and privately on the general principles of physics and experimental optics. Dove was young for a teacher; and his small, elastic, compact figure made him appear younger than he was. At the Jubilee celebration of 1876, to which allusion has already been made, Helmholtz described the subdued delight with which Dove was reading his first announcement on the blackboard of the University, when one of the older students clapped him on the shoulder, and said: "Well, little fellow (*Füchslin*), have you selected the lectures which you wish to hear?" "Yes," he replied, "I shall hear Dove." The older student answered, "That is right good: you will enjoy all his wisdom to yourself."

At Königsberg, Dove's intellectual life was greatly stimulated in



the circle of professors to which he was freely admitted. Bessel's active and brilliant mind fascinated him. At Bessel's house, he met the cousin of his future wife, Adolph Erman (afterwards Bessel's son-in-law), and a friendship was formed which ripened into intimacy when both were afterwards in Berlin. Jacobi, soon to become illustrious as a mathematician, had resided in Königsberg since 1824, and was nearly of the same age as Dove. F. E. Neumann, destined to the place of Professor of Optical Mineralogy, was a *Privat-docent* in 1826. Moser, the future Professor of Physics, and the associate editor with Dove of the first four volumes of the *Repertorium der Physik*, was also a member of this sympathetic group of scientific worthies. Notwithstanding all these congenial surroundings, Dove's heart turned fondly to Berlin, and in 1828 he visited that city to attend the gathering of scientific men under the auspices of Humboldt. Dove's talents were recognized by Humboldt, and a friendship began there and then, which ended only with the life of Humboldt. Dove co-operated with Humboldt in the term-day observations of the magnetic elements for the earth, and he was the first of many others, united in the same work, to publish his observations. The year 1828 was the turning point in Dove's destiny. Then was formed the engagement to the lady whom he married in 1830 at Berlin. Although he had been accustomed from his youth to a simple style of living, a change of residence was soon rendered necessary by the requirements of his family, and, in spite of the remonstrances of the minister Altenstein, he removed to Berlin.

Dove began his new labors by teaching physics and mathematics in the Gymnasium, in a girls' high school, and in the Institute of Technology. In 1841, he succeeded Paul Erman in the Military School and in the School of Artillery. He was soon made Extraordinary Professor of Physics in the University; and, finally, in 1845, Ordinary Professor. But his salary was never large; and he continued his instruction in the Institute of Technology until he was sixty years old, and in the Military School until the year 1877, after paralysis had warned him of his increasing infirmities. The latter position was valuable to him, as it secured for him a residence in the third story of the War Building, where he lived for many years, and where he died.

For half a century, Dove was a hard-working and painstaking teacher. During many of these years he taught general physics in the Gymnasium for eight or twelve hours a week, and to all the classes. Mathematics required of him an equal amount of time. His instruction in the Schools of War and Technology, and in the University,

was given by lectures on physics and meteorology. For the experimental illustration of these lectures he spared no time or labor. He was a familiar sight in the streets of Berlin, as he carried such apparatus as belonged to him from his house, or from one audience to another, in his hand or in a market-basket. But familiarity only deepened the universal respect which his presence always inspired. For a hundred semesters there sat at his feet a succession of interested students, many of whom afterwards, by their own fame, magnified his renown. In the city which had hung with delight upon the lips of Humboldt in 1827-28, the seats and aisles of the largest auditorium were crowded by all ranks of society, to listen to Dove's lectures on meteorology. Germany could not boast of a more clear and eloquent expounder of science, or of a teacher gifted with greater power of infusing his own scientific spirit into those who heard him. Dove was indeed the Faraday and Arago of the scientific and fashionable circles of Berlin.

This learned, laborious, and successful teacher was none the less an original investigator. Two hundred and thirty-six contributions to science between the years 1827 and 1876, published principally in the *Abhandlungen* or the *Monatsberichte* of the Berlin Academy, or in the *Zeitschrift* of the Prussian Statistical Bureau, bear witness to the fertility and originality of his mind. He has left his impress on all the physical sciences, — on electricity and magnetism, on the metric system, acoustics, optics, and optical crystallography. Coronæ, subjective colors, binocular vision, and binaural hearing interested him greatly; and whatever he touched he enriched, not only by his original ideas, but by new instruments of his own happy invention. A differential inductor, a polyphonic siren, a variety of new stereoscopes, a pseudoscope, a photometer, a stephanoscope, his rotating disks for optical deceptions, his complete polarizing apparatus, his rotating polarizer, his new polarizer of Iceland spar, his new analyzer of arragonite, his prisms to produce circular polarization in place of Fresnel's rhombs, his adaptation of the kaleidoscope to the chromatic effects of polarized light, all these ingenious instruments and appliances have made the name of Dove a household word in every well-equipped physical cabinet on both continents. His application of the stereoscope to distinguish a bank-note from its counterfeit, and thereby to detect forgery, is used in many of the banks and offices of Germany.

But it is a greater work to create a new science, especially if it intimately concerns the comfort and safety of mankind, than to extend and illustrate old ones. What, then, are Dove's claims to be called,

as he has been in and beyond Germany, the Father of Meteorology? What passed for meteorology, even within the memory of living men, let the most popular almanacs proclaim. An attempt was made in the last century (almost abortive because it was short-lived) to lay a safe foundation for meteorology by introducing into it the precision and co-operation which had led to such happy results in astronomy; a precision and a co-operation the more imperative and at the same time the more difficult, as the physics of the Globe are more complex than those of the Cosmos. The meteorological society of the Palatinate, organized by Prince Charles Theodore of Mannheim, supplied observers in and out of Germany with uniform instruments, and published their observations in the *Mannheimer Ephemeriden* for 1781-94. The next great awakening on this subject came from Humboldt, for whom every aspect under which the physics of the earth could be contemplated had a profound interest. At his word, numerous meteorological observatories sprang up in the vast territories of the English and Russian empires, also in Europe and America, which supplied him with materials for taking a comprehensive glance at the distribution of the earth's temperature. In imitation of Halley's graphical method of displaying the distribution of terrestrial magnetism, Humboldt constructed isothermal curves, which, by their inclination to the parallels, betrayed their dependence on geographical peculiarities, as well as on astronomical agencies. Dove applied the same construction to each month of the year, handling, for this purpose, vast numbers of observations, many of which required reductions and corrections before they were suitable for comparison.

When, in 1844, Dieterici had been placed at the head of the Prussian Statistical Bureau, Humboldt called his attention to the wants of meteorology, to the defects in the methods of observing, to the crude condition in which observations were often left, and to the incompleteness in the network of meteorological stations. In 1846, Dr. Mahlmann was made Director of the Meteorological Institute of Prussia; but he died in 1848, when he had only begun the needed reforms, and Dove was appointed as his successor. Under Dove's administration old observations were computed (those at Berlin extending back to 1719), affiliated posts for observers were judiciously selected and gradually increased from thirty-one to one hundred and fifty-three, and the results given promptly to the scientific public.

Dove had distinctly in mind three aspects under which the conditions of the atmosphere should be studied: 1. The mean values of the elements; 2. Their periodical changes; 3. Their non-periodical

changes. He discussed particularly the non-periodical changes of temperature, and published his conclusions at five different times between the years 1838 and 1852 in the *Abhandlungen* of the Berlin Academy. He divided the year into seventy-three periods, each five days in length, and computed the mean temperature of every one of them, — a method which was indorsed by the first international congress of meteorologists in 1873. He exploded the notion that the late frosts between the 11th and 13th of May, from which the orangery of Frederick the Great at Sans Souci did not escape, had any wide significance. Though popular tradition associated them with the death or martyrdom of Mamertus, Pancratius, and Servatius, and assigned to them a cosmical origin, the phenomenon was strictly local, and was explained, where it occurred, by the reflex action of a cold district in the neighborhood.

Brandes first broached, in 1820, his centripetal theory of storms, as the result of his study of the weather of 1783. In 1826, he published what he regarded as a confirmation of his views, deduced from the great storm of December 24, 1821. In 1828, Dove re-examined the data which had led Brandes to his conclusion, and maintained that the latter storm was a true whirlwind, revolving against the motion of the hands of a watch, while the storms of the southern hemisphere, which he had investigated, revolved in the opposite direction. Before Dove resumed the subject, Redfield and Reid on the one hand, and Espy on the other, had been engaged in an animated discussion on the merits of the centrifugal and centripetal theories as exemplified in the storms of the Atlantic, the hurricanes of the West Indies, and the typhoons of the Chinese Sea. Dove generously admits, with a candor not always found in scientific men, that Redfield and Reid had reached their conclusions without the aid or knowledge of his own earlier publications on the subject, and he credits them for their rich materials and their independent generalizations, in his "Law of Storms," published in 1841. He says: "But Redfield and Reid, besides placing on a wider basis the rotary movement, which takes place in opposite senses in the two hemispheres, have added, further, some very important observations, the empirical establishment of which is entirely their own; these I shall attempt to connect theoretically with the cyclone movement." He then proceeds to show that the larger whirlwinds, and their opposite characters north and south of the equator, may be evolved from Hadley's general theory of the trade-winds and the transfer of air across parallels of different magnitudes; admitting at the same time that lesser whirls of air and

water, not obedient to the same law of direction, may originate in the conflict of local and accidental winds.

What Dove has called the "Law of Rotation" of the winds has a more universal, though a less boisterous, applicability to the facts of meteorology than his "Law of Storms." Aristotle appears to have had glimpses of this law, according to which all changes of the wind, not local and transitory, followed each other, not at random, but in a regular order, which is reversed for the southern hemisphere. This law declares, in popular language, that there is no permanent change of weather if the wind backs round. Bacon in 1600, and Sturm in 1676, refer to this rule; farmers and navigators are familiar with it. Bacon says: "Si ventus se mutet conformiter ad motum solis . . . non revertitur plerumque, aut, si hoc facit, fit ad breve tempus." As was said at Dove's Jubilee: "For two thousand years men had witnessed the phenomenon without seizing the significance of it." Dove found the explanation in the incessant struggle between the equatorial and polar currents of the same hemisphere, which alternately push each other up and down and from one meridian to another. His educated ear caught in the whisperings or rustlings of the winds the key-note to all the non-periodical changes of the weather; and he elucidated his views by the discussion of thousands of observations of the barometer, thermometer, and hygrometer, extending over fifty years. If Dove gave a wider extension and a more exclusive jurisdiction to Hadley's theory of the trade-winds than all meteorologists would be ready to admit, if he did not allow sufficient scope to the centripetal theory and to antecedent influences which caused the two antagonistic currents to dislodge one another, nevertheless he succeeded in bringing order out of chaos, and in shedding the light of a principle on a confused mass of heterogeneous observations. Truly has it been said: "By his Herculean but well-directed labor he has written his name in large, imperishable characters on the records of science." Dove first appeared before the world as an author in 1827, with a paper on the Winds. This was followed by eight others, all of them on meteorology, and the largest part of his voluminous writings were on the same subject. His last publication in the *Abhandlungen* of the Berlin Academy, was on the weather of 1875-76, and his contribution to the *Jubelband* of Poggendorff was on the meteorological differences between the northern and southern hemispheres. *Par excellence*, Dove was a meteorologist.

Some of Dove's most valuable contributions to journals or transactions were also published as independent works. His "Gesetz der

*Stürme*" passed through four editions in Germany, and was translated into English and French. "*Klimatologie von Nord Deutschland*" appeared in two volumes in 1868-71; the "*Klimatologische Beiträge*," in two parts, in 1859-67; the "*Meteorologische Untersuchungen*," in 1837; "*Ueber Maass und Messen*," two editions, in 1833 and 1835; "*Der Kreislauf des Wassers auf der Oberfläche des Erde*," in 1866, and a translation in 1871; "*Eiszeit, Föhn, und Sirocco*," in 1867; "*Der Schweizerische Föhn*," in 1868; "*Gedächtnissrede auf von Humboldt*," in 1869. Some of his most important works were translated and published in Taylor's Scientific Memoirs, and in a volume of the British Association for 1853. Dove was also the editor or co-editor of eight volumes of "*Repertorium der Physik, 1837-45*," to which he largely contributed.

In 1838 Dove published "*Die neuere Farbenlehre*," which reached a second enlarged edition in 1853, with a somewhat different title. In this book he gives an account of his own original observations and instruments. He repeats in the preface to the second edition his comments on Goethe's criticism of Newton's theory of colors: "For the history of science shows that, notwithstanding the confirmation which observation has given to the wave theory, there never will be wanting, in all time, those to whom the Jesuit Castel is a greater authority than Huyghens, Newton, Fresnel, and Frauenhofer."

Dove was happy in his home. Of four sons and as many daughters, one, a lieutenant in the army, died in 1874 of consumption, induced by the fatigues and exposure of war. Two of his sons he saw elevated to the position of Professors at Göttingen and at Breslau. He himself rejoiced in his work, and none the less in society. In the forenoon, when he was not teaching, he was at his house, and accessible to all. In the afternoon he made a short visit to a confectioner's shop, where he read the papers and took a cup of coffee. But travelling was his chief recreation. His knowledge of modern languages made all societies agreeable and instructive. Often he was sent on delegations by the government. In 1830 he visited Warsaw in the time of the cholera. In 1845 he made a tour of France, England, and Scotland. He was one of the judges at the World's Expositions, in 1851 and 1861 at London, and in 1855 and 1867 at Paris. He attended the scientific associations in Germany, and in 1864 in Switzerland. Every year he visited the meteorological stations in Germany, and occasionally those outside of his own jurisdiction.

Dove was the youngest member and the last survivor of a most brilliant circle of literary and scientific men, who made illustrious the

first period of the University of Berlin; and as such he received its highest honors. He was chosen its Dean and Rector. The government vied with the University in doing him homage. He was Privy-Councillor, and one of the board of examiners for civil and military service. At court his presence was always welcomed, and no gathering of learned men took place in the palace from which he was missing. He was an officer of the *Legion of Honor*, and at his Jubilee in 1876 he received the star of the *Red Eagle Order*. In 1860 he was made a member of the *Ordre pour le Merite*, and in 1867, by the special favor of his high patron, the King, Vice-Chancellor of the *Friedensclasse* of that Order.

Dove was chosen a member of the Berlin Academy in 1837. He was also an Associate of the Berlin Geographical Society, and contributed to its discussions and publications. After the death of Ritter and Barth, he was the most conspicuous member, and at its forty-fifth anniversary he served as its Honorary President. The name of Dove stands upon the rolls of honor of all the brilliant academies of Europe. His merits were early recognized by this Academy, in 1859, when he was elected a Foreign Honorary Member.

## JAMES CLERK MAXWELL.

JAMES CLERK MAXWELL, the only son of John Clerk Maxwell, Esq., was born in 1831 at Middlebie in Scotland. His early education was obtained at the Edinburgh Academy, where he was given the academical club medal for geometry in 1845, and the silver medal for mathematics in 1847. After leaving the Edinburgh Academy, Maxwell entered the University of Edinburgh, and was under the instruction of Kelland, Forbes, and Gregory. In October, 1850, he entered at Peterhouse in Cambridge, and in 1854 was made Second Wrangler and bracketed as First Smith's Prize-man. In December, 1850, he left Peterhouse College and entered his name at Trinity, where, in 1855, he became a Fellow. In 1856, he obtained the Professorship of Natural Philosophy in Marischal College, Aberdeen. In 1860, he succeeded Goodeve as Professor of Natural Philosophy and Astronomy in King's College, London. On the death of his father he retired, in 1865, to his estate in Scotland. In 1871, he accepted the chair of Experimental Physics at Cambridge, and was appointed Director of the Cavendish Physical Laboratory, which was built and equipped under his personal supervision. The American Academy of Arts and Sciences of Boston has the honor

of being the first of the foreign societies to recognize his merit, by electing him, in 1874, a Foreign Honorary Member. He was elected a member of the American Philosophical Society of Philadelphia in October, 1875; Correspondent in the Mathematical Class to the Imperial Academy of Sciences, Göttingen, in December, 1875; Honorary Member of the New York Academy of Science, in December, 1876; Associate of the Amsterdam Royal Academy of Sciences, in April, 1877; and Corresponding Member of the Imperial Academy of Sciences, Vienna, in August, 1877. He was Fellow of the Royal Societies of London and Edinburgh, and of the Cambridge Philosophical Society.

His principal contributions to science are the following:— Paper on the "Motions of Saturnian Rings" in 1857; "On the Theory of Compound Colours, and the Relations of the Colours of the Spectrum," which obtained the Rumford Medal, and was read before the Royal Society, March 22, 1860; "Dynamical Theory of the Electro-magnetic Field, including a Note upon the Electro-magnetic Theory of Light," read before the Royal Society, Dec. 8, 1864; "Viscosity and Internal Friction of Air and other Gases," Royal Society, Feb. 8, 1866; "Dynamical Theory of Gases," May, 1866; "On a Method of making a direct Comparison of Electro-static with Electro-magnetic Force, with a Note on the Electro-magnetic Theory of Light," in June, 1868.

His little treatise on "The Theory of Heat" is the most unexceptional text-book on physics in the English language. After repeated perusals the reader will still find in it new food for thought. Not only are the abstrusest conceptions put in the simplest language, but also theoretical deductions are illustrated by reference to facts of daily experience. In one place, while speaking of superficial tension, he describes how a heated flat-iron can be used to most advantage in causing a piece of paper to remove a grease-spot. The student will find his various essays in the *Encyclopædia Britannica* the best popular sources of information upon "The Atom," "Attraction," "Capillary Action," "Constitution of Bodies," "Diagrams," "Diffusion," "Ether," "Faraday," and "Harmonic Analysis." We have enumerated above only a few of his more important papers. He was a frequent contributor to "Nature," among the pages of which will be found many reviews by him; and it is understood that he left many valuable unpublished papers. The most enduring work left by Maxwell is undoubtedly his treatise on Electricity and Magnetism. Since the appearance of this work a new



school of physicists has arisen, to whom one might justly apply the title of Maxwellites. They have applied the general theorems of Maxwell to special cases in electricity and magnetism, and have adopted his nomenclature and his methods. The treatise is an exhaustive one, and marks a new era in the history of the development of electro-dynamics. The chief characteristic of Maxwell's mathematical methods is their conciseness. Where Continental mathematicians, contemporary with himself, are diffuse, and occupy pages, Maxwell condenses into a few lines. This condensation makes him a difficult author to read. His constant endeavor is to release himself, as he expresses it, "from the thralldom of Cartesian co-ordinates."

Maxwell was in no sense a narrow mathematician. In one place, in his treatise on Electricity and Magnetism, he says: "It was perhaps for the advantage of science that Faraday, though thoroughly conscious of the fundamental forms of space, time, and force, was not a professed mathematician. He was not tempted to enter into many interesting researches in pure mathematics which his discoveries would have suggested if they had been exhibited in a mathematical form, and he did not feel called upon either to force his results into a shape acceptable to the mathematical taste of the time, or to express them in a form which mathematicians might attack. He was thus left at leisure to do his proper work, to co-ordinate his ideas with his facts, and to express them in natural, untechnical language." Throughout his treatise Maxwell constantly refers to the physical conceptions of Faraday, and claims merely to translate these conceptions into mathematical language. Maxwell and Faraday will go down to posterity together: the work of one cannot be fully interpreted without that of the other.

Maxwell was the first physicist to frame an intelligent and comprehensive electro-dynamic theory of Light. This theory is constantly gaining ground, and the day is probably not far distant when the Professor of Optics will need to supplement his course by a consideration of the relations between the phenomena of electricity and those of light. In molecular physics he was regarded as *facile princeps*.

We have thus rapidly glanced at the few facts which are known in regard to the short life of Maxwell. The great public hardly know his name, and the notice taken of his death by his scientific contemporaries seems hardly worthy of his deeds. He was to the scientific world what a Bismarck or a Gladstone is to the political world. He had no time to devote to popularizing science: this labor was left to men better fitted for it. He represents the highest type of a scien-

tific man, and there are very few such men in any century. Those who knew him say that he was a charming companion, and loved conversation. He was frequently consulted upon knotty scientific points, and his talk, which at first was general, began to turn by degrees to the point in question, and gradually the true solution came forth in a manner which seemed to delight himself as much as the propounder of the question. All speak of his keen sense of wit and humor, and here and there in different periodicals can be found little poems which testify to his versatility of mind. He was, moreover, a very religious man, and showed the fulness of his nature by his deep and reverential interest in all the problems of life and mind which are concerned in a belief in a future state.

#### EUGENE EMMANUEL VIOULET-LE-DUC.

THE death of EUGENE EMMANUEL VIOULET-LE-DUC, in the sixty-sixth year of his age, brought to a sudden close a career of remarkable singleness of purpose, independence of character, industry, and success. He was the son of a well-known archæologist and man of letters, who was attached to the court of Charles X., holding the office of Conservateur des Bâtiments Royaux. Our associate early manifested the remarkable powers of observation and delineation which have added such brilliancy to his achievements in letters and in art. It is said that even in his childhood he used to amuse the king with portraits of the personages about the court. He was educated at the Lycée Bourbon; but instead of going to the École Polytechnique, to which he had been destined, and to which the character of his mind seemed particularly to be adapted, he chose to place himself in the atelier of the architect Achille Leclerc. But though he thus seemed to abandon science for art, it soon appeared that the difference was rather in the subject-matter of his study than in the spirit and aim with which it was to be pursued. He soon found that for the purely æsthetic spirit in which the study of architecture was followed at the École des Beaux-Arts he had but little sympathy. The methods which aimed to develop the creative faculty and the powers of design through the cultivation of the taste and imagination were repugnant to him. Architecture, to his mind, was a thing to be investigated, reasoned out, and thoroughly understood; and he believed that it was to be understood only through a scientific study of the constructive processes upon which it is based, and a scientific study of the monuments that have marked its historical development. Refusing, accordingly, to take

part in the exercises and to share the distinctions of a school to which the genius of Duc, Vandoyer, Duban, and Labrousse were already adding a new renown, he turned to the study of the buildings of the Middle Age, the neglect with which they had so long been treated giving to his investigations much of the interest of new discovery together with the zest of a practical protest against that neglect, while the paramount importance of constructive considerations in the development of the mediæval styles rendered them specially congenial to the cast of his mind.

In thus throwing himself out of the beaten track, and in maintaining and defending the isolated position in which he placed himself, it was almost inevitable that he should assume the tone and attitude of a partisan, a relentless critic of commonly received opinions, an uncompromising advocate of newly revealed truths; and this attitude was not, on the whole, perhaps, uncongenial to his vigorous and combative disposition. But if the tone of his numerous writings is pre-eminently polemical rather than judicial, if he too constantly turns aside to decry what he stigmatized as "official art," or to enforce with passionate insistence the necessity of what he considered a "rational" procedure, this must be imputed rather to the conditions of his life, which was one of protest and controversy, than to narrowness of spirit or deficiency of intellectual comprehension. Indeed, he was too truly a man of science not to exhibit, as sooner or later he did not fail to do, a truly catholic appreciation for every form of excellence.

The somewhat solitary position thus assumed was maintained with singular self-reliance and astonishing labor. For twenty years he studied the monumental remains of France, of every period, bringing to their illustration all the light that exhaustive researches among contemporary documents could afford. In this he was greatly aided by the establishment in 1837 of the Commission des Monuments Historiques, of which he was a member. During the next twenty years he gave to the public, in rapid succession, the admirable literary works which will render his name forever famous, in which he embodied the results of these researches, the *Dictionnaire Raisonné de l'Architecture*, in ten volumes; the *Dictionnaire du Mobilier*, in six; the *Entretiens sur l'Architecture*, in two; and the *Histoire de l'Architecture Militaire du Moyen Age*, in one, this last being in part made up from the military articles in the *Dictionnaire*. He also published a series of letters from Sicily; a collection of historical documents under the name of the *Album de Ste. Théodosie*; a work on the cities and ruins of Central America; descriptions of the city of Carcassonne, of the Château de

Coucy, and of the Château of Pierrefonds; a geological and topographical work upon Mt. Blanc, recording the result of observations made during successive summers; a work upon modern fortification; and a volume upon the chapels of Notre Dame de Paris, with details of the decorations as restored by him. Besides these more serious works, he printed from time to time a number of lighter volumes, the work of his leisure hours: "The Story of a House"; "The History of Human Habitations"; "The History of a Fortress"; "The History of a Cathedral and of an Hotel-de-Ville"; and finally, his last work, "How to learn to Draw." These are all thrown into the form of fictitious narrative, in which, as in most examples of historical fiction, it is not always easy to separate what is due to the invention of the writer from what is due to his erudition. He was also a frequent contributor to the artistic journals, publishing, among other things, a series of papers in *L'Art*, upon the subject of restorations.

All these works are profusely illustrated with wood-cuts and engravings, made from drawings by his own hand, of extraordinary variety, beauty, and elaboration of detail.

But if these thirty-three volumes are the best record of his intelligence and learning, they by no means form the substance of his work, nor are the illustrations by which they are embellished the chief examples of his skill. These are rather to be found in the magnificent series of drawings which he executed for the Commission des Monuments Historiques, and those which he from time to time exhibited in the Salon. These comprised, among others, a set of drawings of old French architecture, made at the opening of his career, while still a student with M. Leclerc, which gained for him, at the age of twenty, a medal of the third class. Four years later a medal of the second class was awarded to him for drawings made in Rome, Sicily, and Magna Græcia, including a remarkable view of the city and theatre of Taormina, during the representation of a play. Besides these, he exhibited a restoration of Trajan's Forum, a view of the arcade of the Tuileries in its original estate, and other works, for which he received a first-class medal in 1855, and again in 1878.

He also executed from his own drawings and sketches, aided by his wonderful memory, three remarkable maps of the Maritime Alps, one topographical, one geological, and one showing the roads, houses, and villages; and, at a later period, prepared and published a military map of the works erected during the siege of Paris, accompanied by a text.

These drawings and sketches were made with a facility and precision

indicating a perfect clearness of conception, and a command of hand which was the result of almost incessant practice. The working-drawings and details needed for the execution of his designs were also almost entirely made by his own hand, and many of them were executed upon the works under the eyes of the workmen. Measures have been taken to collect and preserve such of these as can now be recovered.

For these literary and artistic labors were not his only nor his chief occupation. During almost the whole of these forty years he was engaged in the active practice of his profession; not indeed to any great extent in the planning and execution of new buildings, but in the designing and carrying out of a series of restorations, in the course of which a chief part of the most important monuments of mediæval art in France passed under his hand. Beginning with the restoration of the Ste. Chapelle in the palace of St. Louis, in conjunction with MM. Lassus and Duban, and the restoration of the abbey church of Vezelay, he undertook, in rapid succession, important works upon the abbey church of St. Denis, and upon the cathedrals, among others, of Paris, Amiens, Sens, Laon, Chalons sur Marne, Lausanne, and Toulouse. Much of this work, though called restoration, was entirely new, and its great excellence testifies to his powers of design. In original work, however, and in such pure inventions as form the illustrations of the second volume of the *Entretiens*, he was not altogether so happy as where inspired, and to some extent controlled, by the exigencies of archaeological propriety. It is not unlikely that his facility of draughtsmanship served to supersede those slow processes which are needed for the perfecting of an ideal work, and that in this respect he suffered from the lack of that academic training which he so much decried.

Vast and engrossing as were these various labors, they did not entirely occupy his time nor exhaust his spirit. His absolute conviction of the futility and error of the system of architectural instruction pursued at the École des Beaux-Arts necessarily brought with it, in so eager a nature, a desire to improve the administration of the school, and to breathe into it a new life. The sympathetic appreciation of the Count de Nieuwerkerke, obtained for him, in 1863, an opportunity of carrying into practice the reforms he had long desired. In November of that year appeared an imperial decree transferring the direction of the school from the Institute of France to the Minister of Fine Arts. Important changes were at the same time made in the system of administration, and M. Viollet-le-Duc was nomi-

nated Professor of the History of Art and Architecture. The merits of the new scheme were acrimoniously discussed in the journals and pamphlets of the day. But the questions at issue were not destined to be settled upon their merits. The sudden and arbitrary manner in which these changes had been made excited the loyal indignation of the students of the school, who, justly regarding the newly appointed professor as the chief cause of offence, refused to listen to instructions which, under other circumstances, they would have received with interest and respect. Moreover, the government, by a supplementary decree, issued in January, 1864, hastened to make such explanations and modifications as served, in his eyes, to deprive the new rules of all their value. He at once sent in his resignation, published under the name of *Entretiens* the discourses he had prepared for his classes, and proceeded to organize, in conjunction with his friend M. Trélat, a civil engineer of great intelligence, an independent school, in which the views he had so strenuously advocated should be systematically carried out. In this school, to which the name of *École Centrale d'Architecture* was given, he continued to take an active interest, forming one of its board of governors, and preparing for its students, with his own hand, a series of examples for exercises in draughtsmanship, which have since been published, of unusual interest and great technical excellence. He had also previously, for eight years, taken personal charge of the instruction in ornamental drawing in the *École Impériale du Dessin*.

It only remains to say that the range of his knowledge and skill was not limited to the art which he professed, nor even to the useful and ornamental arts ancillary to architecture, in which he constantly showed himself capable, not only of giving advice to his workmen, but of showing them with his own hands how best their work should be done. He seemed to understand everything, as one of his workmen expressed it, from astronomy to cooking. It is said that while the court of Louis Napoleon was at Compiègne, he was often summoned from his work at Pierrefonds to act as master of the revels, to contrive the scenic entertainments, arrange the music, design the costumes, and paint the scenery. When the Empire fell, he devoted his powers and attainments to the service of his country, organizing a corps of civil engineers, auxiliary to the military arm. In this he held the office of lieutenant-colonel, and during the siege of Paris worked night and day, walking stick in hand, directing the repair of the works as they were destroyed by the enemy's fire. Upon the return of peace, he for the first time began to take an active interest in

public affairs, ardently espousing the cause of the Republic, and writing constantly for the press, generally in the *XIX. Siècle*, a series of articles upon public affairs, many of them directed against the Society of Jesus, in which his historical learning, literary skill, and firmness of conviction are alike conspicuous. His election as a member of the Municipal Council of Paris enabled him to take an active part in the administration of public business, and it is probable that, had his life been prolonged, he would presently have been returned to the Chamber of Deputies.

But as these new interests and duties, which already had seemed to draw him away from the field of his life's labors, were beginning to open before him a new career of usefulness and honor, death suddenly intervened. He died at his country-house in Lausanne, on the 17th of September, 1879. He was born in Paris, on the 27th of January, 1814.

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Since the last Report the Academy has received an accession of ten new members, as follows: four Resident Fellows, F. A. Gooch, N. D. C. Hodges, E. S. Wood, and W. L. Richardson; four Associate Fellows, J. W. Gibbs, Clarence King, A. S. Packard, Jr., and J. C. Watson; two Foreign Honorary Members, Georg Curtius, in place of F. W. Ritschl, and Sir James F. Stephen, at large. On the other hand, in consequence of permanent removal from the State, Jules Marcou and Horatio R. Storer have abandoned their fellowship. The list of the Academy, corrected to the date of this Report, is hereto added. It includes 191 Resident Fellows, 95 Associate Fellows, and 72 Foreign Honorary Members.

# LIST

## OF THE FELLOWS AND FOREIGN HONORARY MEMBERS.

### FELLOWS.—191.

(Number limited to two hundred.)

#### CLASS I.—*Mathematical and Physical Sciences.*—63.

##### SECTION I.—7.

###### *Mathematics.*

W. E. Byerly,	Cambridge.
Benjamin A. Gould,	Cambridge.
Gustavus Hay,	Boston.
Benjamin Peirce,	Cambridge.
James M. Peirce,	Cambridge.
John D. Runkle,	Boston.
Edwin P. Seaver,	Boston.

##### SECTION II.—10.

###### *Practical Astronomy and Geodesy.*

J. Ingersoll Bowditch,	Boston.
Alvan Clark,	Cambridgeport.
George B. Clark,	Cambridgeport.
Henry Mitchell,	Roxbury.
Robert Treat Paine,	Brookline.
E. C. Pickering,	Cambridge.
William A. Rogers,	Cambridge.
Arthur Searle,	Cambridge.
L. Trouvelot,	Cambridge.
Henry L. Whiting,	Boston.

##### SECTION III.—31.

###### *Physics and Chemistry.*

John Bacon,	Boston.
A. Graham Bell,	Boston.
John H. Blake,	Boston.
Thos. Edwards Clark,	Williamstown.
W. J. Clark,	Amherst.
Josiah P. Cooke,	Cambridge.
James M. Crafts,	Boston.
Charles R. Cross,	Boston.
William P. Dexter,	Roxbury.
Amos E. Dolbear,	Medford.
Charles W. Eliot,	Cambridge.
Moses G. Farmer,	Newport.

Wolcott Gibbs,	Cambridge.
F. A. Gooch,	Cambridge.
Augustus A. Hayes,	Brookline.
Henry B. Hill,	Cambridge.
N. D. C. Hodges,	Cambridge.
Eben N. Horsford,	Cambridge.
T. Sterry Hunt,	Boston.
Charles L. Jackson,	Cambridge.
Joseph Lovering,	Cambridge.
William R. Nichols,	Boston.
John M. Ordway,	Boston.
Robert H. Richards,	Boston.
Edward S. Ritchie,	Boston.
S. P. Sharples,	Cambridge.
Frank H. Storer,	Jamaica Plain.
John Trowbridge,	Cambridge.
Cyrus M. Warren,	Brookline.
Charles H. Wing,	Boston.
Edward S. Wood,	Cambridge.

##### SECTION IV.—15.

###### *Technology and Engineering.*

G. R. Baldwin,	Woburn.
John M. Batchelder,	Cambridge.
C. O. Boutelle,	Washington.
Henry L. Eustis,	Cambridge.
James B. Francis,	Lowell.
John B. Henck,	Boston.
E. D. Leavitt, Jr.,	Cambridgeport.
William R. Lee,	Roxbury.
Hiram F. Mills,	Lawrence.
Alfred P. Rockwell,	Boston.
Stephen P. Ruggles,	Boston.
Charles S. Storrow,	Boston.
William R. Ware,	Boston.
William Watson,	Boston.
Morrill Wyman,	Cambridge.



CLASS II. — *Natural and Physiological Sciences.* — 65.

## SECTION I. — 8.

*Geology, Mineralogy, and Physics of the Globe.*

Thomas T. Bouvé,	Boston.
William T. Brigham,	Boston.
Algernon Coolidge,	Boston.
John L. Hayes,	Cambridge.
Charles T. Jackson,	Boston.
William B. Rogers,	Boston.
Nathaniel S. Shaler,	Cambridge.
Charles U. Shepard,	Amherst.

## SECTION II. — 11.

*Botany.*

George B. Emerson,	Boston.
William G. Farlow,	Boston.
George L. Goodale,	Cambridge.
Asa Gray,	Cambridge.
H. H. Hunnewell,	Wellesley.
Thomas P. James,	Cambridge.
John A. Lowell,	Boston.
C. S. Sargent,	Brookline.
Chas. J. Sprague,	Boston.
Edward Tuckerman,	Amherst.
Sereno Watson,	Cambridge.

## SECTION III. — 23.

*Zoölogy and Physiology.*

Alex. E. R. Agassiz,	Cambridge.
J. A. Allen,	Cambridge.
Robert Amory,	Brookline.
Nath. E. Atwood,	Provincetown.
James M. Barnard,	Boston.
Henry P. Bowditch,	Boston.
Edward Burgess,	Boston.
Samuel Cabot,	Boston.
John Dean,	Waltham.

Hermann A. Hagen,	Cambridge.
C. E. Hamlin,	Cambridge.
Alpheus Hyatt,	Cambridge.
Wm. James,	Cambridge.
Samuel Kneeland,	Boston.
Theodore Lyman,	Boston.
Edward S. Morse,	Salem.
L. F. Pourtales,	Cambridge.
Frederic W. Putnam,	Cambridge.
James J. Putnam,	Boston.
Samuel H. Scudder,	Cambridge.
D. Humphreys Storer,	Boston.
Henry Wheatland,	Salem.
James C. White,	Boston.

## SECTION IV. — 23.

*Medicine and Surgery.*

Samuel L. Abbot,	Boston.
Henry J. Bigelow,	Boston.
Henry I. Bowditch,	Boston.
Benjamin E. Cotting,	Roxbury.
F. W. Draper,	Boston.
Thomas Dwight,	Boston.
Robert T. Edes,	Roxbury.
Calvin Ellis,	Boston.
C. F. Folsom,	Boston.
Richard M. Hodges,	Boston.
Oliver W. Holmes,	Boston.
R. W. Hooper,	Boston.
Alfred Hosmer,	Watertown.
Edward Jarvis,	Dorchester.
Francis Minot,	Boston.
Edward Reynolds,	Boston.
J. P. Reynolds,	Boston.
W. L. Richardson,	Boston.
George C. Shattuck,	Boston.
J. Baxter Upham,	Boston.
Charles E. Ware,	Boston.
John C. Warren,	Boston.
Henry W. Williams,	Boston.

CLASS III. — *Moral and Political Sciences.* — 63.

## SECTION I. — 17.

*Philosophy and Jurisprudence.*

J. B. Ames,	Cambridge.
C. S. Bradley,	Cambridge.
Phillips Brooks,	Boston.
James F. Clarke,	Jamaica Pl.
Richard H. Dana,	Boston.
C. C. Everett,	Cambridge.
John Fiske,	Cambridge.
Horace Gray,	Boston.
J. C. Gray, Jr.,	Boston.
L. P. Hicock,	Northampton.
O. W. Holmes, Jr.,	Boston.
Mark Hopkins,	Williamstown.
C. C. Langdell,	Cambridge.
John Lowell,	Boston.
Henry W. Paine,	Cambridge.
Theophilus Parsons,	Cambridge.
J. B. Thayer,	Cambridge.

## SECTION II. — 15.

*Philology and Archæology.*

Ezra Abbot,	Cambridge.
W. S. Appleton,	Boston.
William P. Atkinson,	Boston.
H. G. Denny,	Boston.
Epes S. Dixwell,	Cambridge.
William Everett,	Quincy.
William W. Goodwin,	Cambridge.
Ephraim W. Gurney,	Cambridge.
Bennett H. Nash,	Boston.
Chandler Robbins,	Boston.
John L. Sibley,	Cambridge.
E. A. Sophocles,	Cambridge.
John W. White,	Cambridge.
Justin Winsor,	Cambridge.
Edward J. Young,	Cambridge.

## SECTION III. — 17.

*Political Economy and History.*

Chas. F. Adams, Jr.,	Quincy.
Henry Adams,	Boston.
Edward Atkinson,	Boston.
Charles Deane,	Cambridge.
Charles F. Dunbar,	Cambridge.
Samuel Eliot,	Boston.
George E. Ellis,	Boston.
E. L. Godkin,	Cambridge.
William Gray,	Boston.
Edward Everett Hale,	Boston.
H. C. Lodge,	Boston.
Francis Parkman,	Brookline.
A. P. Peabody,	Cambridge.
J. S. Ropes,	Boston.
Nathaniel Thayer,	Boston.
Henry W. Torrey,	Cambridge.
Robert C. Winthrop,	Boston.

## SECTION IV. — 14.

*Literature and the Fine Arts.*

Charles F. Adams,	Boston.
George S. Boutwell,	Groton.
J. Elliot Cabot,	Brookline.
Francis J. Child,	Cambridge.
Ralph Waldo Emerson,	Concord.
John C. Gray,	Cambridge.
Henry W. Longfellow,	Cambridge.
Charles G. Loring,	Boston.
James Russell Lowell,	Cambridge.
Charles Eliot Norton,	Cambridge.
Thomas W. Parsons,	Wayland.
Charles C. Perkins,	Boston.
H. H. Richardson,	Brookline.
John G. Whittier,	Amesbury.

ASSOCIATE FELLOWS. — 95.

(Number limited to one hundred.)

CLASS I. — *Mathematical and Physical Sciences.* — 39.

SECTION I. — 8.

*Mathematics.*

Charles Avery, Clinton, N.Y.  
E. B. Elliott, Washington, D.C.  
William Ferrel, Washington, D.C.  
Thomas Hill, Portland, Me.  
Simon Newcomb, Washington, D.C.  
H. A. Newton, New Haven, Conn.  
James E. Oliver, Ithaca, N.Y.  
T. H. Safford, Williamstown, Mass.

SECTION II. — 18.

*Practical Astronomy and Geodesy.*

S. Alexander, Princeton, N.J.  
W. H. C. Bartlett, Yonkers, N.Y.  
J. H. C. Coffin, Washington, D.C.  
Wm. H. Emory, Washington, D.C.  
Asaph Hall, Washington, D.C.  
J. E. Hilgard, Washington, D.C.  
George W. Hill, Nyack, N.Y.  
Elias Loomis, New Haven, Conn.  
Maria Mitchell, Poughkeepsie, N.Y.  
C. H. F. Peters, Clinton, N.Y.  
George M. Searle, New York.

J. C. Watson, Ann Arbor.  
Chas. A. Young, Princeton, N.J.

SECTION III. — 12.

*Physics and Chemistry.*

F. A. P. Barnard, New York.  
John W. Draper, New York.  
J. W. Gibbs, New Haven, Conn.  
S. W. Johnson, New Haven, Conn.  
John Le Conte, Berkeley, Cal.  
A. M. Mayer, Hoboken, N.J.  
W. A. Norton, New Haven, Conn.  
Ogden N. Rood, New York.  
H. A. Rowland, Baltimore.  
L. M. Rutherford, New York.  
Benj. Silliman, New Haven, Conn.  
J. L. Smith, Louisville, Ky.

SECTION IV. — 6.

*Technology and Engineering.*

Henry L. Abbot, New York.  
A. A. Humphreys, Washington, D.C.  
John Rodgers, Washington, D.C.  
Wm. Sellers, Philadelphia.  
George Talcott, Albany, N.Y.  
W. P. Trowbridge, New York.

CLASS II. — *Natural and Physiological Sciences.* — 27.

SECTION I. — 14.

*Geology, Mineralogy, and Physics of the Globe.*

George J. Brush, New Haven, Conn.  
James D. Dana, New Haven, Conn.  
J. W. Dawson, Montreal, Canada.  
Edward Desor, Neuchâtel, Switz.  
J. C. Fremont, New York.

F. A. Genth, Philadelphia.  
Arnold Guyot, Princeton, N.J.  
James Hall, Albany, N.Y.  
F. S. Holmes, Charleston, S.C.  
Clarence King, Washington, D.C.  
Joseph Le Conte, Berkeley, Cal.  
J. Peter Lesley, Philadelphia.  
R. Pumpelly, Newport, R.I.  
Geo. C. Swallow, Columbia, Mo.

## SECTION II. — 8.

*Botany.*

A. W. Chapman, Apalachicola, Fla.  
 G. Engelmann, St. Louis, Mo.  
 Leo Lesquereux, Columbus, Ohio.

## SECTION III. — 9.

*Zoölogy and Physiology.*

S. F. Baird, Washington, D.C.  
 C. E. Brown-Séquard, Paris.  
 J. C. Dalton, New York.

J. L. LeConte, Philadelphia.  
 Joseph Leidy, Philadelphia.  
 O. C. Marsh, New Haven, Conn.  
 S. Weir Mitchell, Philadelphia.  
 A. S. Packard, Jr., Providence.  
 St. Julien Ravenel, Charleston, S.C.

## SECTION IV. — 1.

*Medicine and Surgery.*

W.A. Hammond, New York.

CLASS III. — *Moral and Political Sciences.* — 29.

## SECTION I. — 8.

*Philosophy and Jurisprudence.*

D. R. Goodwin, Philadelphia.  
 R. G. Hazard, Peacedale, R.I.  
 Nathaniel Holmes, St. Louis, Mo.  
 James McCosh, Princeton.  
 Charles S. Peirce, New York.  
 Noah Porter, New Haven, Conn.  
 Isaac Ray, Philadelphia.  
 Jeremiah Smith, Dover, N.H.

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 F. E. Church, New York.  
 R. S. Greenough, Florence.  
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Max Müller,	Oxford.
H. A. J. Munro,	Cambridge.
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## SECTION IV.—3.

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